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TEXTILE RESEARCH JOURNAL

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The Gravimetric Estimation of Medulla in Wool

D. A. Ross and J. B. Speakman

Department of Textile Industries, The University, Leeds, England

Abstract

A gravimetric estimation of the amount of medulla in wool can be made by determining the amount of residue left after samples of known dry weight have been treated with a 1.6% solution of peracetic acid for 48 hr. at 25° C., followed by a 1.0 *N* solution of ammonia for 24 hr. at 25° C. A correction must be applied for the amount of residue given by nonmedullated wools, which is approximately the same for Merino and crossbred wools. Samples which are to be used for analysis should not be dried at a high temperature before use, because the amount of residue increases with increasing temperature of drying, especially when the moisture content of the wool is high, owing to the formation of resistant cross-linkages between the peptide chains.

Introduction

The usual method of estimating the amount of medulla in wool is based on Elphick's observation [4] that nonmedullated fibers are almost invisible when immersed in benzene, whereas medullated fibers are white and clearly visible because of the air pockets in the medulla. In McMahon's adaptation [7] of this test, a known weight of wool is spread thinly and evenly over a defined area under benzene, and the light scattered in a vertical direction by the medulla is measured by means of a photocell. The instrument is known as a medullometer. It gives a general indication of the degree of medullation of different wools and has, therefore, been used extensively, in both the original and the modified form [2], by a fleece-testing organization in New Zealand. The exact significance of the "photoelectric index" (P.I.) of medullation is not, however, clear. When McMahon calibrated the original instrument, he used five wools with different degrees of medullation and obtained a linear relationship between the percentage air space, calculated from the specific gravity of the samples, and the P.I. This is surprising, because the amount of light scattered by the medulla should be proportional to its area rather than its volume, and Ross [8] has, in fact, shown recently that there is a highly significant correlation between the medulla area per unit weight and the P.I. ($n = 24$, $r = 0.94$). He found also that the test is not a reliable measure of the percentage of medullated fibers ($r = 0.59$), owing to the disproportionate effect of a few large fibers, the percentage of fibers with a medulla greater than 20μ in width being highly correlated with the P.I. ($r = 0.85$). These and other observations suggest that the exact significance of the photoelectric index of medullation cannot be determined without

the help of an independent method of estimating the amount of medulla in wool. Various considerations suggested that a gravimetric method might be developed, and it was hoped, during the course of the work, to discover the most suitable means of isolating medulla for chemical examination.

Since the medulla of animal fibers is deficient in sulfur, one obvious line of attack on the problem is to make use of reactions which lead to the production of solubilizing groups from cystine bonds. It is probable that Lloyd and Marriott's isolation of medulla from goat hair [6] by means of a 4 *N* solution of sodium hydroxide is based on this principle, but since alkalis promote fission of peptide as well as disulphide bonds, no sharp discrimination between the medulla and cuticle plus cortex can be expected. Dilute solutions of sodium sulfide should be more effective, because the reduction of cystine cross-linkages in cuticle and cortex to give solubilizing cysteine side chains is less likely to be accompanied by the formation of new cross-linkages, e.g., lanthionine, and there is less danger of peptide bond fission. It has been observed also [3] that medulla can be isolated by treating medullated wool with a 1.0 *M* solution of thioglycollic acid in phenol hydrate for 24 hr. at 65° C., but peptide bond hydrolysis may be more pronounced than with, say, dilute solutions of sodium sulfide in the cold. Perhaps the most promising basis for a gravimetric method of estimating medulla is to use performic or peracetic acid [1] to convert cystine cross-linkages into cysteic acid side chains, because the reagents are believed not to attack peptide bonds, and preferential dissolution of the oxidized cuticle and cortex should be brought about by dilute alkalis. It is not to be expected that the medulla alone will be isolated by such a procedure, because a residue consisting of epicuticle and other cell membranes is left when nonmedullated fibers are treated with peracetic acid and then with ammonia [1], but if the amount of such a residue is the same for different wools, a gravimetric estimate of medulla would be possible. The relative merits of all these methods of isolating and estimating medulla were examined in the following experiments.

Experimental

Preliminary Experiments

(*a*) *Purification of wool.* In a preliminary survey of the various possible methods of isolating and estimating medulla, three types of wool were used, viz., Australian 64s Merino, New Zealand 48s crossbred which was almost completely free from medulla, and a highly medullated Scotch Blackface wool. Pigmented fibers and most of the fine, nonmedullated, undercoat fibers were removed from the Blackface wool. In addition, the exposed tips of the staples of all the wools were cut off, the intact root ends being purified by extraction with ether for 24 hr. in a Soxhlet apparatus, followed by teasing to remove foreign matter, and then by extraction with alcohol for 24 hr. The wools were afterward washed in running water for 24 hr. and conditioned in the humidity room (65% R.H., 72° F.). As the Blackface wool was so heterogeneous, the purified fibers were cut into 1-cm. lengths, which were well mixed before samples were taken for analysis.

(*b*) *Preparation of reagents*

(i) *Sodium hydroxide.* Solutions of 0.75 and 4.0 *N* were prepared from the A.R. reagent, the concentrations being adjusted, when necessary, after titration with hydrochloric acid.

(ii) *Sodium sulfide.* Two solutions of approximately 1 and 5% concentration were prepared from A.R. sodium sulfide, the exact concentrations, as determined by the method of Vogel [10], being 0.94 and 4.74%, respectively.

(iii) *Thioglycollic acid in phenol hydrate.* After the purity of the thioglycollic acid had been determined by the method of Klason and Carlson [5], a 1.0 *M* solution of thioglycollic acid in phenol hydrate was prepared.

(iv) *Peracetic acid.* The purity of the reagent (Laporte Chemicals Ltd.) was determined by the method of Smit [9], and a 1.6% (w/v) solution, containing not more than 0.12% of hydrogen peroxide, was used to oxidize the wool, which was afterward treated with a 1.0 *N* solution of A.R. ammonia.

(c) *Procedure*

Some 30 to 40 0.3-g. samples of each type of conditioned wool were weighed out, two of the samples being dried to constant weight over phosphorus pentoxide *in vacuo* to determine the regain and thus allow the dry weights of the remaining samples to be calculated. Each sample was treated with the chosen reagent in a B.24 stoppered test tube, which was kept at the desired temperature by means of a water thermostat, and the liquor : dry wool ratio was 100 : 1

in all cases. Treatment with the solution of thioglycollic acid in phenol hydrate was carried out at 60° C., but the other reagents were used at 25° C. Although agitation increases the rate of dissolution, the contents of the test tubes were not shaken at any stage, and the residues which remained after different times of treatment were collected in tared sintered glass crucibles of porosity 3. During washing, no suction, or only very slight suction, was used in order to avoid both loss of severely degraded residues and choking of the filters. Finally, the crucibles and residues were dried to constant weight at 105° C. Features of the experimental methods which are peculiar to the different reagents are given below.

(i) *Sodium hydroxide.* The residues were each washed with 200 ml. of distilled water before being dried.

(ii) *Sodium sulfide.* In early experiments the residues were washed first with sodium chloride solution to reduce the swelling, but this procedure was discontinued when it was found that the swollen residues were less likely to choke the filter. Thereafter, the residues were merely washed with 200 ml. of distilled water before being dried.

(iii) *Thioglycollic acid in phenol hydrate.* After the desired time of treatment, the contents of the test tube were centrifuged and the supernatant liquid was filtered through a sintered glass crucible under slight suction. The residue was then washed into the crucible with 10 ml. of phenol hydrate. After the centrifuge tube and reaction tube had each been washed with 10 ml. of phenol hydrate, the residue was finally washed with 200 ml. of absolute alcohol and dried.

(iv) *Peracetic acid–ammonia.* After oxidation with the solution of peracetic acid for the desired time, the wool was transferred to a 50-ml. sintered glass crucible, porosity 1, and then washed with 500 ml. of distilled water. Subsequent treatment with 1.0 *N* ammonia for 24 hr. at 25° C. was carried out in a stoppered test tube, the residue being transferred to a sintered glass crucible and washed with 200 ml. of distilled water before drying.

(d) *Results*

The amounts of residue left after different times of treatment with the various reagents are summarized in Tables I to IV.

TABLE I. Effect of Treatment of Wools with Sodium Hydroxide

Concentration of sodium hydroxide, normality	Time of treatment, hr.	Residue (% on dry weight) from		
		Merino	Crossbred	Blackface
4.0	1	18.3	—	—
	3	5.8	16.3	12.4
	6	0.8	2.4	8.7
	9	0.1	0.1	8.2
	12	—	0.1	7.9
	18	—	0.2	6.7
0.75	6	43.5	40.8	38.6
	12	15.1	17.2	21.1
	18	8.5	10.1	16.1
	24	5.2	7.7	13.4
	36	2.3	3.3	9.8
	48	1.1	2.5	8.5
	72	0.7	1.0	7.9
	96	0.7	0.4	7.3
	120	0.2	0.2	7.2

While the nonmedullated wools are dissolved by 4.0 *N* sodium hydroxide in 9 hr., the Blackface wool gives a residue of over 8%. On examination under the microscope, the medulla which is thus isolated was found to be partly degraded, but the impression of degradation is enhanced by the separation of the

TABLE II. Effect of Treatment of Wools with Sodium Sulfide

Concentration of sodium sulfide, %	Time of treatment, hr.	Residue (% on dry weight) from		
		Merino	Crossbred	Blackface
4.74	3	16.2	16.2	26.3
	6	11.5	11.5	16.8
	12	8.8	7.2	15.1
	18	5.4	3.3	10.1
	24	2.3	2.1	8.5
	36	0.8	0.1	6.2
0.94	6	35.3	38.1	37.9
	12	22.1	30.1	33.9
	18	19.7	26.7	29.6
	24	15.9	22.5	26.6
	36	13.6	16.2	23.4
	48	12.6	11.9	22.1
	72	10.3	9.5	19.1
	96	9.9	7.3	18.0
	120	7.9	6.1	16.4
	144	7.0	5.5	15.6
	192	5.3	4.6	13.5
	216	—	3.9	13.2
	240	4.2	3.8	11.6

medulla into small groups of cells. A much longer time is needed to dissolve the nonmedullated wools in 0.75 *N* sodium hydroxide, but although the amount of residue left by the Blackface wool after 120-hr. treatment is less than after 9-hr. treatment with 4.0 *N* sodium hydroxide, microscopic examination suggests that the isolated medulla is intact.

With the more concentrated solution of sodium sulfide the difference between the amounts of residue from medullated and nonmedullated wools reaches a limiting value of about 6% after 24-hr. treatment. Under the microscope the medulla appears to be intact up to 18-hr. treatment, but is severely degraded in 36 hr., when the nonmedullated wools are almost completely dissolved. The concentrated solution of sodium sulfide is not, therefore, regarded as a suitable reagent for either the isolation or estimation of medulla. For times of treatment beyond 48 hr., there is at first a roughly constant difference between the amounts of residue left by medullated and nonmedullated wools in the 0.94% solution of sodium sulfide. Under the microscope the medulla isolated in this way is surrounded by a transparent sheath and appears to be intact. It seems probable, therefore, that the dilute solution of sodium sulfide is a satisfactory reagent for the isolation and estimation of medulla.

The crossbred wool is dissolved much more slowly than the Merino wool, and it is only after more than 48-hr. treatment that the residue from the former falls below that from the Blackface wool. After 10-day treatment the residue from the nonmedullated wools falls almost to zero, and the medulla isolated from the Blackface wool in this time seems under the microscope to be intact.

Similar amounts of residue are obtained from crossbred and Merino wools after 48-hr. treatment with peracetic acid, followed by ammonia, and the difference between the amounts of residue from the Blackface and the nonmedullated wools is approximately constant after the same time of treatment. Further, the medulla appears under the microscope to be unaffected by treatment with peracetic acid and ammonia.

Although the peracetic acid–ammonia method, unlike treatment with a dilute solution of sodium sulfide or with a solution of thioglycollic acid in phenol hydrate, gives a residue in which the medulla is heavily contaminated with epicuticle and other cell membranes, it seems to provide the most convenient basis for a gravimetric estimation of medulla because the necessary time of treatment with peracetic acid is relatively short.

TABLE III. Effect of Treatment of Wools with Thioglycollic Acid in Phenol Hydrate

Time of treatment, hr.	Residue (% on dry weight) from		
	Merino	Crossbred	Blackface
3	61.8	80.8	71.7
6	28.1	55.3	42.8
12	25.4	43.6	36.2
18	21.9	36.5	31.6
24	21.1	34.0	27.5
36	17.0	27.8	25.4
48	15.8	27.0	24.1
72	13.5	19.4	23.6
96	10.1	14.7	21.2
120	5.2	12.1	20.2
168	2.4	8.0	17.5
240	0.8	2.0	13.6

TABLE IV. Effect of Treatment of Wools with Peracetic Acid–Ammonia

Time of treatment, hr.	Residue (% on dry weight) from		
	Merino	Crossbred	Blackface
3	27.6	50.7	30.5
6	21.5	25.5	27.8
12	17.3	22.0	27.9
18	15.1	17.9	27.1
24	15.0	15.4	24.8
36	14.0	15.4	25.1
48	13.8	13.2	24.1
72	14.1	12.7	23.4
96	12.2	11.4	22.4
120	10.4	11.6	21.9
168	10.2	10.2	21.0
240	10.3	9.9	20.3

Estimation of Medulla in Benzol-Tested Samples

A series of 22 benzol-tested N-type Romney wool samples was provided by Dr. F. W. Dry of New Zealand, two from each of 11 bulk samples. Before the tested samples were examined, a further comparison of the preceding methods of isolating and estimating medulla was undertaken with the bulk samples. After the wools had been purified by extraction with alcohol and ether, followed by washing in water, five samples were withdrawn from each for treatment with (a) 4.0 *N* sodium hydroxide for 9 hr., (b) 0.75 *N* sodium hydroxide for 5 days, (c) 4.74%

sodium sulfide for 24 hr., (d) 0.94% sodium sulfide for 14 days, and (e) 1.6% peracetic acid for 48 hr., followed by 1.0 *N* ammonia for 24 hr. The results are given in Table V, which includes values for the P.I. of the wools, these being averages of the results obtained with the two tested samples in each case.

In all cases there is a general tendency for the amount of residue to increase with increasing P.I., but the most sensitive method of estimating medulla is that using peracetic acid and ammonia, apart perhaps from treatment with the dilute solution of sodium sulfide, which is far more tedious. It is obvious, too, that there is a close relationship between the amounts of residue given by the peracetic acid–ammonia procedure and the P.I. of the wools. This treatment was, therefore, used with the 22 benzol-tested samples, and the results are given in Table VI.

TABLE V. Residues after Various Treatments Applied to Romney Wools

Sample No.	P.I.	Residue (% on dry weight) after NaOH 4.0 *N*	NaOH 0.75 *N*	Na_2S 4.74%	Na_2S 0.94%	Peracetic acid–ammonia
310	14.2	0.5	1.1	0.2	1.8	14.0
84	21.2	0.7	1.0	1.1	1.9	15.7
11	31.6	1.1	1.6	1.9	2.5	15.8
243	39.4	0.8	2.0	1.9	2.8	16.5
28	44.7	1.5	2.1	2.2	3.9	16.9
59	68.0	2.2	2.8	2.2	3.6	17.7
70	71.8	2.0	2.9	2.8	4.5	17.9
322	74.5	1.9	3.3	3.6	4.0	17.9
76	79.6	1.9	3.1	3.0	5.1	18.2
89	87.3	2.3	4.7	4.2	5.8	20.3
321	89.9	2.2	4.6	4.3	6.6	19.8

TABLE VI. Relationship between Residue given by Peracetic Acid–Ammonia Treatment and the Photoelectric Index (P.I.) of Romney Wools

Sample No.	P.I.	Residue, % on dry weight
310a	13.1	14.1
310b	15.3	13.9
84b	20.1	16.1
11b	21.5	15.4
84a	22.3	15.3
28a	32.7	16.3
243a	37.5	17.0
243b	41.3	15.9
11a	41.7	16.1
28b	56.6	17.5
322a	64.0	17.7
70b	64.1	17.9
59b	66.0	17.6
59a	70.0	17.9
89a	78.4	20.1
76a	78.5	17.2
70a	79.4	18.0
76b	80.6	19.2
321b	81.3	19.5
322b	84.9	18.1
89b	96.1	20.5
321a	98.5	20.1

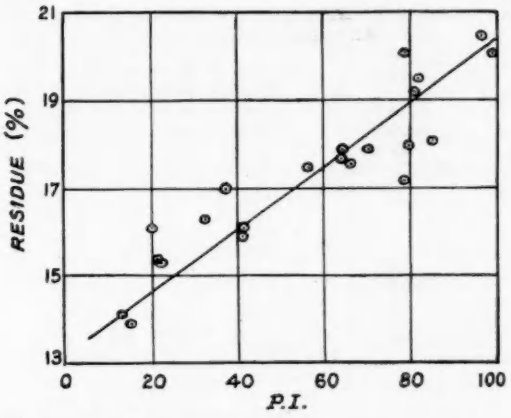

Fig. 1. Relationship between residues after treatment and photoelectric index of wools.

The correlation between the P.I. and the residue weight is very high ($r = 0.92$), and the relationship between the two is shown in Figure 1.

Effect of Drying Conditions on the Amount of the Peracetic Acid–Ammonia Residue

During the further use of the peracetic acid–ammonia method of estimating medulla, it was found that another series of benzol-tested N-type Romney wools gave residues of 20 to 70%. Unfortunately, the previous history of this abnormal series of wools was unknown, but since treatments which lead to the formation of new cross-linkages between the peptide chains of wool had been found to result in abnormally high residues [3], it seemed likely that the wools had been modified during previous examination in New Zealand. It was unlikely that they had been treated with alkali, but they might have been dried at a high temperature, and the effect of different conditions of drying on the amount of the peracetic acid–ammonia residue was, therefore, examined.

(i) *Time of heating.* Samples of crossbred wool, which either had a regain of 14.1% or had been dried

TABLE VII. Effect of Heat Followed by Peracetic Acid–Ammonia Treatment.

Time of heating, hr.	Residue (% on dry weight) from wool heated at 14.1% regain	Residue (% on dry weight) from wool heated at Dryness
0.5	15.2	—
1	16.4	15.3
2	15.9	—
3	16.9	16.0
6	15.2	—
12	15.6	15.7
24	16.9	—
180	16.4	15.4

to constant weight over phosphorus pentoxide *in vacuo*, were heated in an electrically heated oven at 90° C. for periods up to 180 hr. The wools were then treated with a 1.6% solution of peracetic acid for 24 hr., followed by the 1.0 *N* solution of ammonia for 24 hr., and the amounts of residue isolated are given in Table VII.

In general, the residues given by wools dried from 14.1% regain are higher than those from wools heated in the dry state, but the differences are small. Further, the amount of residue seems to be independent of the time of heating at 90° C.

(ii) *Temperature of drying.* Samples of crossbred wool (16.0% regain) were oven-dried for 6 hr. at temperatures ranging from 90° to 150° C. The amounts of residue left after the wools had been treated with peracetic acid and ammonia under the same conditions as before are given in Table VIII.

At temperatures above 120° C. there is a rapid increase in the amount of residue with rise of drying temperature up to at least 140° C.

In agreement with the hypothesis that high residues are due to the formation of resistant cross-linkages between the polypeptide chains, heating was found to diminish the supercontraction of crossbred fibers in peracetic acid. The root ends of heated and untreated fibers were mounted in setting frames, drawn just taut, and their lengths measured. After the fibers had been slackened, the frames were immersed in the solution of peracetic acid for 24 hr. at 25° C. The fibers were then washed overnight in running water, conditioned in room air for 8 hr., drawn taut, and remeasured. Average values for the supercontraction are given in Table IX.

TABLE IX. Effect of Heat on Supercontraction

Temperature, ° C.	Supercontraction, %
Untreated	21.1
130	13.7
140	10.9

(iii) *Regain.* From first principles it seemed probable that the amount of residue obtained from heated wools would increase with increasing regain. Samples of crossbred wool, which had either been conditioned (C) to a regain of 16% at 22.2° C., or saturated (S) with distilled water at room temperature, were dried (D) over phosphorus pentoxide *in vacuo* for 48 hr. at 90° C. In certain cases, the treatments were repeated several times in succession, and the residues obtained from the various samples are given in Table X.

Discussion

It seems clear from the preceding experiments that the best methods of isolating medulla for chemical examination are (a) treatment with a 0.94% solution of sodium sulfide for 10 days at 25° C. and (b) treatment with a 1.0 *M* solution of thioglycollic acid in phenol hydrate for 10 days at 60° C. When medullated fibers are treated with peracetic acid, followed by ammonia, the residue consists of medulla contaminated with epicuticle and other membranes,

TABLE VIII. Effect of Temperature of Drying

Temperature, ° C.	Residue, % on dry weight
90	15.2
105	15.9
110	15.6
120	16.8
130	34.8
140	53.8
150	54.3

TABLE X. Effect of Drying from Various Regains on Residues

Treatment	Residue, % on dry weight
C.D.	15.8
S.D.	19.4
C.D., C.D.	20.3
C.D., S.D.	26.6
S.D., S.D.	43.3
S.D., S.D., S.D., S.D.	49.1

and this procedure does not provide a suitable means of isolating medulla. Since, however, nonmedullated Merino and crossbred wools give approximately the same amount of residue after treatment with peracetic acid and ammonia (Table IV), the greater amounts of residue obtained from medullated wools provide a basis for the gravimetric estimation of medulla. The amounts of residue are closely correlated with the photoelectric indices of the wools, as shown in Table VI and Figure 1, and the absence of a precise relationship is believed to be due to the fact that the photoelectric index is not simply related to either the area, volume, or weight of medulla. For routine analysis, however, the photoelectric assessment of medullation will always be preferred because of the speed with which measurements can be made, and it is, therefore, satisfactory that there should be a close connection between the weight of medulla and the photoelectric index.

As the amount of residue obtained from any wool after treatment with peracetic acid and ammonia increases with the temperature of drying and the regain from which it is dried, as shown in Tables VIII and X, it is clearly desirable that the dry weights of samples which are to be used for analysis should not be determined directly, but should be calculated from the measured regains of samples weighed out at the same time as those used for analysis.

Acknowledgment

One of the authors (D.A.R.) is indebted to the New Zealand Wool Board for a scholarship which enabled him to take part in the investigation.

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The Mechanism of Carrier Action in Dyeing Dacron Polyester Fiber

M. J. Schuler

Organic Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.[1]

DACRON polyester fiber was introduced to the textile market by du Pont in 1950. Since that time, many millions of pounds of this new fiber have been dyed by two principal methods: (1) It has been dyed at temperatures above 100° C. in pressure vessels. (2) It has been dyed at temperatures of 100° C. or lower by adding organic compounds called carriers to the dye bath to increase the dyeing rate.

In a search for carriers, it was found empirically that many organic compounds increased the rate of dyeing [3]. It is agreed by some that this increase in the rate of dyeing resulted from an increase in the rate of dye diffusion through the fiber. There is disagreement, however, on the mechanism by which this is accomplished. Vickerstaff [5] summarized some of the current ideas as follows: (1) Small polar compounds, such as phenol, diffuse readily into Dacron polyester fiber and are absorbed by hydrogen bonding. Being hydrophilic, these compounds then attract water molecules into the fiber, leading to swelling and greater ease of diffusion. (2) Hydrophobic dyeing assistants, such as benzene, biphenyl, and chlorobenzene, could act in one of two ways. The original theory considered the carrier to be a compound that literally carries the dye into the fiber by complex formation. A later idea suggested that the carriers decrease polymer interchain forces, reducing internal viscosity, and thus permitting greater dye diffusion rates.

Quite a different position is taken by Choquette [1]. He suggested that chlorobenzene promoted faster dyeing of Dacron polyester fiber by producing a layer of concentrated dye solution around the fiber thereby promoting absorption and penetration.

Zimmerman [8] also does not believe that swelling is important in the mechanism of carrier action. He proposed that the dye is soluble in the carrier in the monomolecular state. The rate of dyeing is therefore increased because single molecules diffuse into the fiber more rapidly than dispersed aggregates of dye molecules.

[1] Contribution No. 224 from Jackson Laboratory.

Waters [7] discussed the efficiency of carriers. He theorized that the distribution of carriers between the fiber and the aqueous dye bath is important in carrier activity. Fern and Hadfield [2] suggest that water-soluble carriers plasticize the fiber. Water-insoluble carriers plasticize the fiber, and in addition surround the fiber with a solvent layer in which dye is highly soluble. Dyeing rate is then further accelerated by the increased concentration gradient.

All of the work on the carrier dyeing of Dacron reported in the literature has been carried out in aqueous dye baths. Neither the dyes nor the carriers are usually completely soluble in water. Thus, it is difficult to specify their concentrations, and to compare them on an equal basis.

The present investigation is concerned with carrier-dyeing phenomena in an essentially non-aqueous system (isoöctane saturated with water), where homogeneity of the dye bath phase permits specification of carrier and dye concentration.

The results obtained can best be interpreted on the basis that water (which is a powerful carrier) and the various organic carriers increase the internal mobility of the Dacron polymer chains and thereby increase diffusibility of dye molecules within the fiber phase. The rate of diffusion of dye molecules in the fiber is controlled by the dye activity in the bath, and not its concentration.

The present work was initiated to determine whether a common denominator existed for carriers; whether the carrier effectiveness could be predicted. In order to accomplish this objective the carrier, the dye, and the vehicle must be completely miscible over the range of concentrations to be studied. Then the concentrations can be specified. To achieve complete miscibility, we used isoöctane as a dye bath vehicle. Isoöctane is almost ideal; it is an excellent solvent for dyes and carriers; it has practically no solubility in Dacron, and it has little or no effectiveness as a carrier.

Carrier dyeing was investigated as if there were two separate phases in the carrier dyeing process:

the rate of solution and equilibration of the carrier and the fiber; the rate of solution and equilibration between the dye and the fiber which had already been treated with the carrier. This rather idealized system is not the same as a practical dye bath, for in our experimental system the partition of carrier and dye took place between iso-octane and Dacron polyester fiber instead of between water and Dacron. The partition coefficients are vastly different in the two systems, and there is another difference: in a commercial dye bath the solution of carrier and dye in the Dacron occurs almost concurrently. However, the results of our work should be applicable to commercial systems.

Experimental

Dye Chamber

The Jackson Laboratory Kinetodyeograph was developed expressly for studying the rate of dyeing. This all stainless steel unit is schematically shown in Figure 1. A detailed description will be published later. The unit is electrically heated by external heating tapes, and the temperature is regulated by manually controlling the voltage. The pump circulates the dye bath either through the yarn package or directly back to the bath according to the setting of a rapidly acting valve. The bath and fiber can thus be brought to thermal equilibrium before the bath is circulated through the yarn package. The Kinetodyeograph is so constructed that the process of dyeing can be followed by spectrophotometric determination of the dye concentration in the bath, and by sampling of the fiber through a special port in the top. For the work reported in this paper, the fiber was sampled and analyzed, because the concentration of the carrier and the dye in the bath did not change by more than 2%.

Dye bath

The isoöctane (2,2,4-trimethylpentane) used as the dye bath vehicle was the standard ASTM rating fuel obtained from Phillips Petroleum Company. Its purity was 99.6 mole per cent; its boiling point was 99.3° C. To the isoöctane were added carriers, dyes, and in many cases, water.

Carrier or Dyeing Assistant

The following carriers were used in this study:

1,2,4-Trichlorobenzene	Dow Chemical Company, distillation range 214–217° C.; 99% trichlorobenzene by Cl analysis
Biphenyl	Eastman Kodak, White Label
Phenylmethylcarbinol	Carbide and Carbon Chemical Corp.
Methyl benzoate	Eastman Kodak, White Label
o-Phenylphenol	Eastman Kodak, White Label
Acetophenone	Eastman Kodak, White Label

Dye

Two dyes were used: a red dye, 1-amino-4-hydroxyanthraquinone and a yellow dye, N^1: N^4-diphenyl-3-nitrosulfanilamide. The red dye was a commercial dye base (purity 95%) containing no diluent. The yellow dye was a laboratory preparation used and described in earlier work [4].

Fiber

The Dacron polyester fiber was staple yarn 2/26 (2 ply, 26 count), which had a fiber diameter of 17

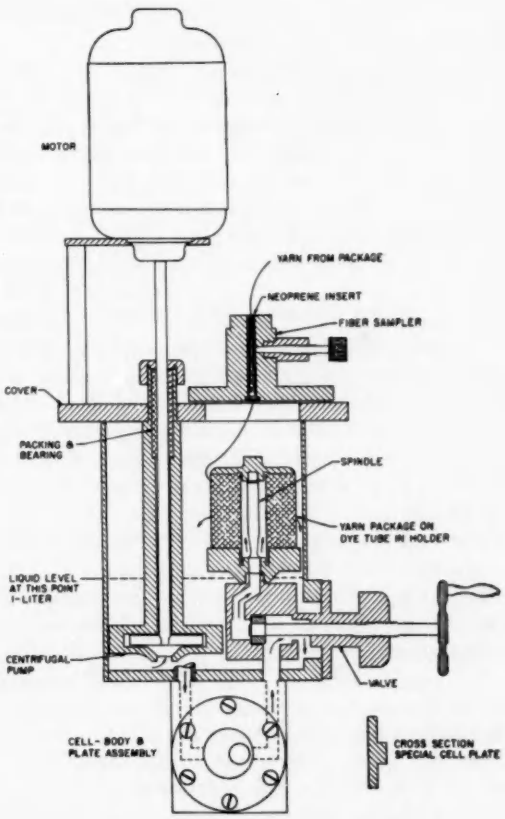

Fig. 1. The Kinetodyeograph.

microns. The yarn was wound with minimum tension on tared perforated stainless steel spools by using a Universal winder (model 50), a 2-in. cam, and a soft package attachment. The packages were extremely soft (Durometer 0). Dacron required soft packages, for the yarn shrinks appreciably during the dyeing, and this causes considerable package tightening. When the extremely soft packages were used, the packages were dyed within 5% of uniformity from the center to the outside; this was true even for the most rapid processes studied.

Dyeing Procedure

A. Application of Carrier

One liter of the isoöctane dye bath (dry or saturated with H_2O) containing the carrier was brought to 95° ± 0.5° C., and the fiber package, preheated to 95°, was introduced. After thermal equilibrium was reestablished, the operator opened the valve and the bath flowed through the package. Samples averaging 0.4 g. were taken periodically.

B. Application of Dye

After equilibrating the fiber with the carrier, as described above, circulation to the package was stopped, dye was added to the bath and was completely dissolved. Thermal equilibrium was then reestablished, and the bath was again circulated through the package, as in A above.

Fiber Sampling and Analysis

The Kinetodyeograph was operated under 40-lb. gauge nitrogen. When the fiber sample valve was opened, the escaping nitrogen carried the fiber sample with it. Thus, the fiber could be rapidly sampled and at the same time cooled. The fiber was immediately rinsed in H_2O, blotted, rinsed in ice cold acetone, blotted, air dried, and weighed. The above procedure could be repeated with no change in fiber weight within a ± 0.2-mg. weighing error.

The weight of the carrier in the fiber was determined by heating the fiber-carrier sample to constant weight in an oven at 120° C.

The weight of the dye in the fiber was determined spectrophotometrically by using a chlorobenzene extract of the fiber, as described in [4].

Results and Discussion

The dyes and carriers were completely soluble in the isoöctane medium; this permitted accurate specification of the concentrations and the distribution of the components at equilibrium. Surprisingly, the dyeing rate in isoöctane was only a fraction of the rate in water. However, by adding water to the isoöctane system, we obtained a rate six times that in isoöctane alone and comparable with an aqueous system. Figure 2 shows this effect of water on the rate of dyeing Dacron polyester fiber with a nonionic dye in isoöctane. Water also increased the rate of diffusion of the carriers into Dacron. The data for phenylmethylcarbinol in Figure 3 represent the characteristics of the carriers studied. For phenylmethylcarbinol, water increased the diffusion rate by a factor of three. One concludes from these results that water is an excellent carrier. It is therefore fortunate that Dacron is not completely hydrophobic. The concentration dependence of water as a carrier was not determined, for water diffuses so rapidly through the fiber that an accurate measurement of the weight of water in the fiber could not be made. Experimental data [6] extrapolated to 95° C., however, indicated that about 1% of water could be absorbed by Dacron at 100% relative humidity. This 0.5 molal solution of water in Dacron is effective as a carrier.

Concentration is another factor which controls the

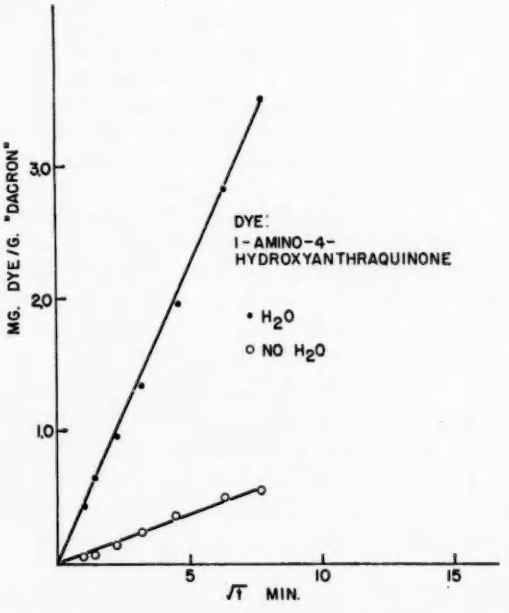

Fig. 2. Effect of H_2O on dye diffusion into Dacron from isoöctane, 95° C.

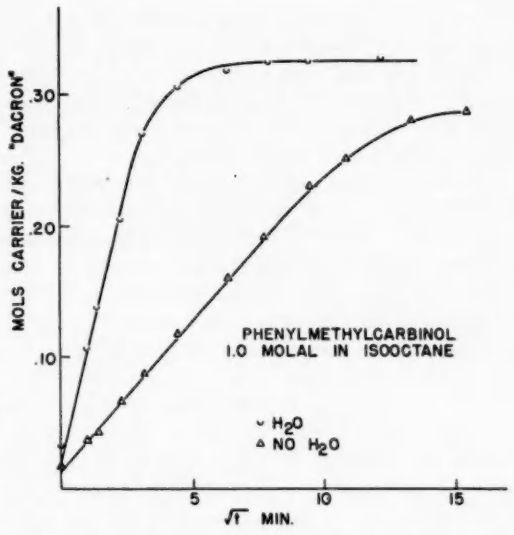

Fig. 3. Effect of H_2O on carrier diffusion into Dacron from isoöctane, 95° C.

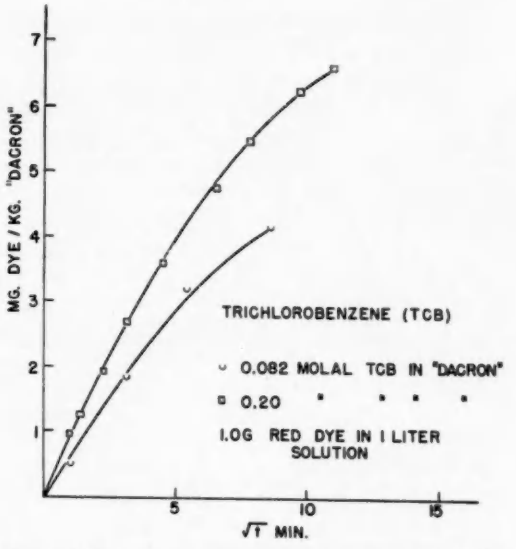

Fig. 5. Effect of carrier concentration on dye diffusion into Dacron, 95° C.

rate of carrier diffusion into Dacron polyester fiber. Figure 4 shows the increase in the rate of carrier diffusion with the increase in carrier concentration. The dotted straight lines drawn through the data intersect at progressively shorter times as the concentration of the carrier increases. This example for methyl benzoate is representative of the carriers studied.

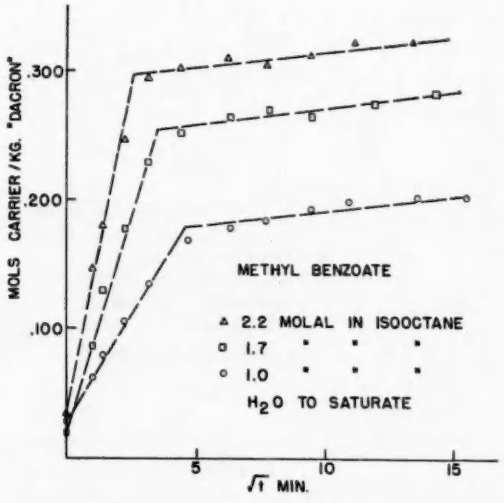

Fig. 4. Effect of carrier concentration on carrier diffusion into Dacron, 95° C.

When the concentration of the carrier in the bath and in the fiber increased, then the rate of dyeing increased, as shown in Figure 5. These results do not adequately demonstrate the effect because the activity of the dye was not held constant. The red dye used was much more soluble in trichlorobenzene than in isoöctane. Therefore, as the concentration of the carrier increased, while the concentration of the dye remained constant, the activity of the dye decreased. This effect will be discussed later. The increase in the rate of dyeing as a function of the increase in carrier concentration, has been adequately demonstrated by others in practical aqueous systems.

Since the concentration of the carrier in the dye bath controls not only the carrier's own rate of diffusion in the fiber but also the rate of the dye diffusion, some bench mark must be established for comparing one carrier with another. In this research the molal concentration of the carrier in the fiber was used. The concentration of the carrier in the isoöctane solution was adjusted so that the concentration in Dacron polyester fiber was about 0.3 molal, as shown in Table I.

By adjusting the concentration of carriers in Dacron to a comparable molality, one can compare the effect of an equal number of molecules on the rate of dyeing. However, little can be said regarding the relative rates of carrier diffusion, because the concentrations in the bath were different.

TABLE I. Concentration of Carrier in Dacron at Equilibrium

Carrier	Conc. in bath (molal)	Conc. in fiber (molal)
Acetophenone	1.0	0.27
Methyl benzoate	2.2	0.32
o-Phenylphenol	0.46	0.32
Phenylmethylcarbinol	1.0	0.33
Trichlorobenzene	2.9	0.31

TABLE II. Saturation Values 1-Amino-4-Hydroxyanthraquinone in Dacron Polyester Fiber at 95° C.

Carrier	Dye in fiber, mg./g.
Acetophenone	23.3
Methyl benzoate	21.9
0-Phenylphenol	22.4
Phenylmethylcarbinol	23.1
Trichlorobenzene	21.7

In order to evaluate the carriers on a comparable basis, the dye activity has to be the same in all cases. We could work at saturation and be assured of equal activity, but this would involve a large amount of dye as well as the difficulty of ensuring a saturated solution, and complete removal of solid dye from yarn. A more convenient method would be to operate at the same fraction of saturation. Table II shows the level of dyeing at equilibrium obtained from saturated dye solutions in the carrier concentrations specified in Table I. The red dye, 1-amino-4-hydroxyanthraquinone was used.

The solubility of dye in Dacron polyester fiber for all cases is close, and for our purposes it may be considered equal. If we could then adjust the dye concentration in each of these media, so that the resulting dyeing at equilibrium would be the same fraction of the saturation value, then the activity of the dye in the bath in all cases would be equal. Accordingly, the dye bath concentration was adjusted so that at equilibrium the amount of dye in the fiber was about $\frac{1}{3}$ of the saturated value. For each carrier, a package of Dacron polyester fiber was equilibrated to about 0.3 molal concentration and then dyed to one third its saturation value. The results are given in Figure 6. From this figure one can see that although widely different carrier classes were used (a chlorinated benzene, a phenol, an ester, a ketone, and an alcohol), the rate of dyeing is relatively independent of the type of carrier. Similar results are shown in Figure 7 for the carrier dyeing of Dacron using the yellow dye N^1,N^4-diphenyl-3-nitrosulfanilamide. Also shown is the large increase in the carrier activity of phenylmethylcarbinol when water is present.

The controlling factor in the rate of carrier dyeing is the concentration of the carrier in the Dacron when constant dye activity is maintained. The concentration of a carrier in Dacron is determined by its solubility in the dye bath and its solubility in Dacron. The ratio of the solubilities is the partition coefficient of the carrier between Dacron and the dye bath when the coefficient is constant.

Since the spread in effectiveness of the carriers (Figures 6 and 7) is small, one is led to the conclusion that they are working, in large part, by the same mechanism. that despite the differences in their functionality, the mechanism of carrier activity varies little. The mechanism appears to be the loosening of polymer interchain forces (either weak dipole forces or van der Waal's forces) with a resulting increase in the diffusion rate of both the carrier and the dye. However, the carriers that are hydrogen bond donors (phenylmethylcarbinol and o-phenylphenol) are slightly more efficient and this slight difference may be due to diminishing or eliminating

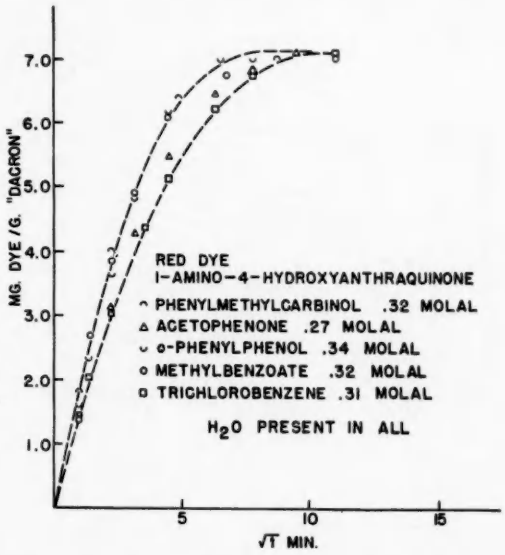

Fig. 6. Effect of carriers on rate of dye diffusion in Dacron, 95° C.

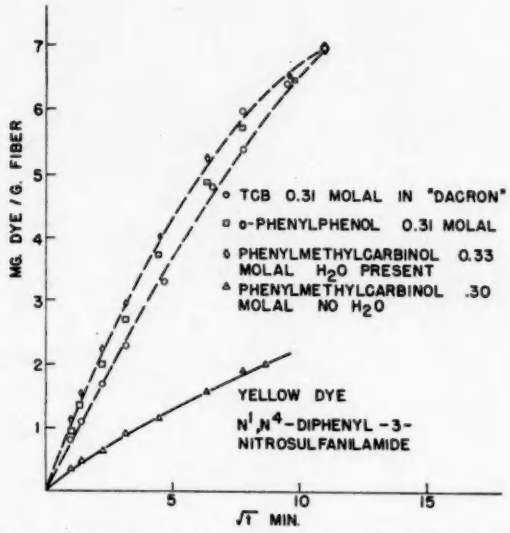

Fig. 7. Effect of carriers on rate of dye diffusion in Dacron, 95° C.

any attractive forces between hydrogen and oxygen in Dacron polyester fiber.

Table III lists the solubilities of several organic compounds in Mylar polyester film at 95° C. Mylar and Dacron are chemically and structurally similar; therefore, the solubility in Mylar should be proportional to the solubility in Dacron. The results in the table permit the following rationalization of carrier activity. In an aqueous bath the partition coefficient for dimethylformamide and Cellosolve favors the water so markedly (completely miscible), that the concentration in the Dacron is very low.

TABLE III. Solubilities of Carrier in Mylar Polyester Film at 95° C.

	Solubility, %
Anisole	7.4
Acetophenone	10.0
Benzaldehyde	9.7
Benzamide	3.6
Benzoic acid	6.8
Benzylalcohol	8.5
Cellosolve	3.7
Phenyl Cellosolve	9.1
Chlorobenzene	8.4
Trichlorobenzene	13.0
Dimethylformamide	6.4
Dimethyl terephthalate	3.8
Methyl benzoate	10.0
o-Phenylphenol	22.0
Phenylmethylcarbinol	8.0

Thus their carrier activity is usually not detected. Dimethyl terephthalate is satisfactory commercially. Its ultimate activity however, is controlled by its low solubility in the fiber. Compounds more soluble in Dacron polyester fiber are more effective carriers; these include chlorobenzene, benzoic acid, benzaldehyde, anisole, trichlorobenzene, and o-phenylphenol. Their ultimate activity is high due to relatively high molar solubility in the fiber. In order to obtain the high fiber concentration, the bath concentration in some cases must also be high, at the start of a dyeing. Commercially this situation causes quality problems. Some of the possible candidates are not acceptable commercially because of their cost, toxicity, and spotting.

The selection of carrier candidates would be less empirical if more was known about predicting solubilities. Those chemical structures having high molar solubilities in Dacron and low solubilities in water, could be selected and thus large partition coefficients in favor of the fiber could be obtained. Since our rules of solubility and partition are insufficiently developed at this time, carrier selection must still be relatively empirical. The requirements are known; the means are obscure.

The work reported here was carried out in a predominantly organic dye bath. The carrier and dye diffusion processes were separated in order to determine the mode of carrier action. In the practical aqueous dye bath, both processes occur simultaneously. The above statements regarding rates must therefore be modified to include the rate of carrier diffusion. Since the rate of carrier diffusion is so much greater than that of dyes, this modification is almost negligible. The fundamentals of carrier action as summarized in the conclusions should apply to aqueous systems.

Conclusions

The dyeing of Dacron polyester fiber with carriers and dyes proceeds by the following steps:

1. Equilibration of the surface layer of Dacron with organic carrier, water, and dye.
2. Diffusion of organic carrier and water into the fiber; this loosens the interchain forces.
3. Diffusion of dye through the somewhat more permeable fiber.

The above steps are concentration dependent. All other things being equal, the greater the carrier con-

centration within the fiber, the more rapid the dye penetration. Carriers also assist the diffusion of other carriers.

The diffusion of dyes into the fiber depends on the activity of the dye in the system and not on the concentration in any one phase.

The principles presented here are applicable to all Dacron, carrier, and dye–dye bath systems.

Acknowledgment

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The Soiling Characteristics of Textile Fibers
Part III: The Effect of Twist on Soil Retention

A. S. Weatherburn and C. H. Bayley

Textile Research Section, National Research Council, Ottawa, Canada

Abstract

The effect of twist on soil retention has been studied for a series of acetate yarns containing 34 filaments of 3.5 den./filament. With increasing twist, soil retention first increased to a maximum, and then decreased to values below that of the untwisted yarn. Microscopic examination of the soiled yarn indicated that at 20 turns/in. visible soil particles had penetrated to the center of the yarn, whereas at 60 turns/in. the soil was located on the exterior surface only.

THE retention of soil by textile materials is influenced by many factors, some of which have been discussed in previous publications in this series [5, 6].

It is generally recognized [1, 2, 3, 4] that one mechanism of soil retention involves mechanical entrapment of soil particles in interfiber spaces, i.e., between two or more adjacent fibers or filaments. It seemed probable that the quantity of soil held by this means would be influenced by the amount of twist in the yarn, but as far as could be ascertained, quantitative measurements of the effect of twist on soil retention have not been reported in the literature. The purpose of the present paper is to provide such data for one specific yarn.

Materials and Method

The yarns used are listed in Table I. These were bright, continuous filament, acetate yarns containing 34 filaments of 3.5 den./filament, and were all identical except for the amount of twist. The variation in yarn denier is due to contraction on twisting. The

TABLE I. Description of Yarns Used

Designation	Twist, turns/in.	Yarn denier
A-0	0	120
A-20	20	125
A-40	40	134
A-60	60	140

yarn was extracted for 24 hr. in a Soxhlet apparatus with benzene, dried, rinsed thoroughly with distilled water, dried, and conditioned at 70 ± 2° F. and 65 ± 2% R.H.

The soil, soiling method, and evaluation technique were identical with those described in the previous paper [6]. Stated briefly, the yarn was soiled with screened vacuum cleaner soil, the excess soil was removed by rotation in a perforated dusting cage, and the soil content was estimated by dissolving the soiled yarn in acetone and measuring the optical density of the resulting suspension. Since the same dispersing medium was used throughout, no correction was made for the effect of the solvent on the readings obtained. The results are given in terms of "effective soil content," i.e., the weight of soil retained multiplied by the specific absorbance of the soil, expressed in relative units.

The soil retention of the various yarns was measured at soiling levels of 0.5, 1.0, 1.5, and 2.0, the "soiling level" being defined as 10(weight of soil)/(weight of yarn). The results are given in Figures 1 and 2.

Discussion

The curves given in Figure 1 show the usual linear relationship between log soil content and log soiling level. It is apparent that the amount of twist not only influences the soil retention at a given soiling level, but also influences the slope of the line. Over the range from 20 to 60 turns/in., the amount of soil retained by the yarn decreases with increasing twist, this effect being more pronounced at the higher soiling levels. It is interesting to note, however, that the A-20 yarn retains more soil than the untwisted yarn. This is illustrated more clearly in Figure 2. The portions of the curves between zero twist and 20 turns/in. are shown as dotted lines since the contours of the curves in this region are not based on experimentally determined points. However, in order to draw a smooth curve through the points it is necessary to assume a fairly rapid increase in soil retention at very low twists. It is quite possible that the maximum soil retention may be considerably higher than shown, as indicated by the alternative dotted line in the top curve. This is of interest in relation to the interpretation of certain data given in the previous paper [6]. It was found that, in general, soil retention increased with decreasing filament denier for any one type of yarn. There were, however, a few cases where the soil retention was too high

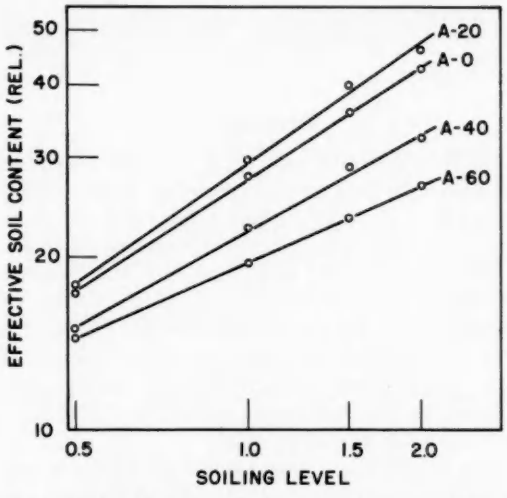

Fig. 1. Soil retention versus soiling level for various degrees of twist.

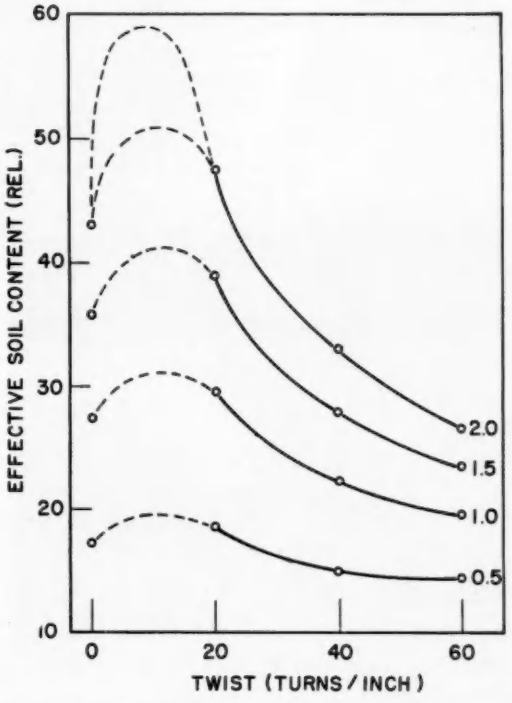

Fig. 2. Soil retention versus twist for various soiling levels.

to conform with the general trend. While the amount of twist in all the yarns studied was comparatively low, it was observed that those yarns that showed abnormally high soil retention also had a somewhat higher twist. The data given in Figure 2 provides a plausible explanation for the previously observed facts.

The effect of twist on soil retention was further clarified by microscopic examination of the A-20 and A-60 soiled yarns. By mounting the specimens in glycerine (which has a refractive index very close to that of the acetate fiber), the transparency of the fiber was increased and the soil particles were more readily seen. Figure 3 shows the same yarn (A-60) in a dry (*air*) mount (a) and in a glycerine mount (b). Owing to the transparency of the fiber, it was also possible to focus the microscope on different planes through the thickness of the yarn. Figure 4 shows the location of soil on the A-60 yarn. For Figure 4a the microscope was focussed on the top surface of the yarn close to one side. Soil particles can be seen over the entire surface of the yarn. The fuzziness at the top of the picture is caused by the curvature of the yarn surface which makes it impossible to get the whole field of view in sharp focus at one time.

Without moving the slide the microscope was then focussed on the bottom surface of the yarn [Figure 4c]. Again it will be noted that soil particles are visible over the entire field of view. The difference in filament angle in Figures 4a and 4c shows conclusively that opposite surfaces of the yarn are being viewed. For Figure 4b the microscope was focussed exactly half way between the two previous settings, i.e., on a plane through the center of the yarn. Soil particles are visible on the external surface of the yarn (top of the photograph) but the interior of the yarn appears to be completely free of visible particles. Hence in the tightly twisted yarn, A-60, the visible soil is located entirely on the external surface and has not penetrated to any extent into the interior of the yarn.

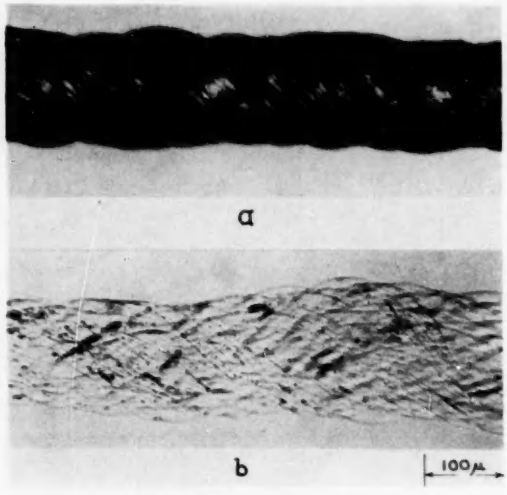

Fig. 3. A-60 soiled yarn: (a) air mount, (b) glycerine mount.

Figure 5 shows a similar series of photomicrographs of the A-20 soiled yarn. The top and bottom surfaces resemble those of the previous yarn, but the condition at the center plane (Figure 5b) is quite different. In this case soil particles are visible throughout the whole field. Comparison of the magnification in Figures 3 and 5 indicates that, in Figure 5, the center of the yarn is on a line located roughly one third of the vertical dimension of the picture from the bottom, i.e., the field of view includes more than half the width of the yarn. Hence it may be concluded that soil has penetrated to the center of the A-20 yarn.

It should be noted also that soil which penetrates to the interior of a twisted yarn is protected from external influences, and hence is not readily removed, for example, in the dusting operation. In an untwisted yarn the soil would be expected to penetrate to the interior, but it would also be more readily removed. Hence the data given in Figure 2 are in accord with the conclusions from the microscopic examination.

Conclusions

As the amount of twist in a yarn increases from zero twist, the soil retention increases rapidly at low values of twist owing to the entrapment of soil in the spaces between filaments or fibers throughout the whole interior of the yarn. This soil is not readily dislodged by external influences. With further increase in twist the soil retention reaches a maximum and then gradually decreases as the interior of the yarn becomes inaccessible to the soil particles, and soil holding sites become limited to those located on the external surface of the yarn.

For the particular yarns studied the maximum soil retention appears to occur at a twist of between zero and 20 turns/in. and would be expected to vary for

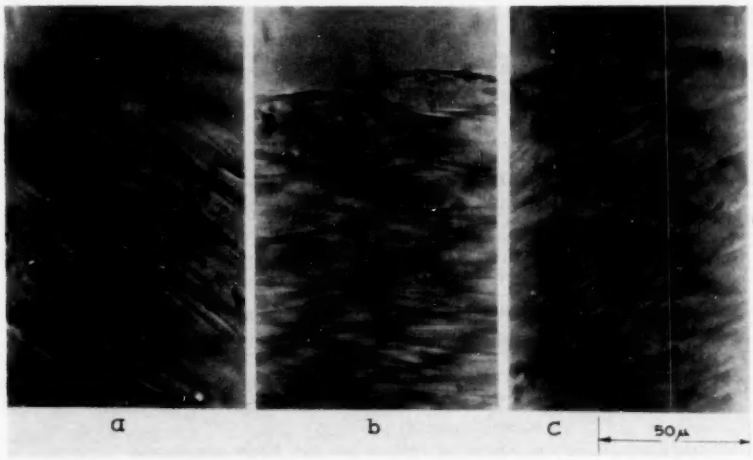

Fig. 4. A-60 soiled yarn: (a) top surface, (b) center, (c) bottom surface.

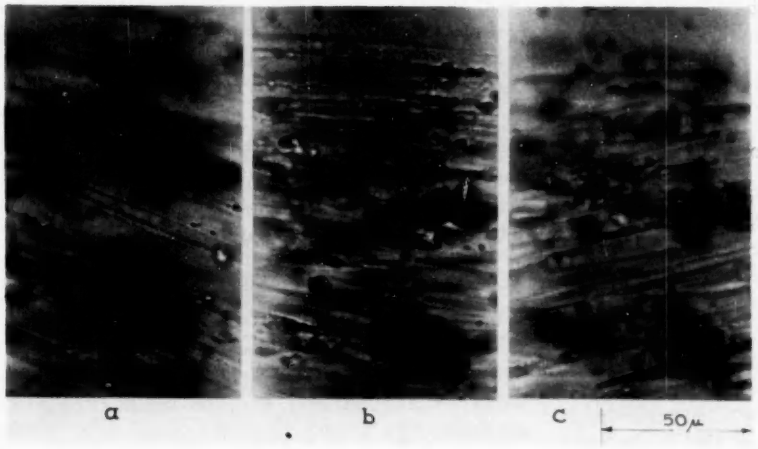

Fig. 5. A-20 soiled yarn: (a) top surface, (b) center, (c) bottom surface.

yarns differing in number of filaments and in filament denier.

Acknowledgment

The authors are indebted to Canadian Celanese Ltd., Drummondville, Quebec, for supplying the yarns used in this work.

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Cotton Fibers as Means of Transmitting Water Vapor[1]

Lyman Fourt, R. Allan Craig, and Marjorie B. Rutherford

Harris Research Laboratories, Washington, D.C.

Abstract

The water vapor transmission of fibers can be measured independent of any air space surrounding the fibers, by using sections cut from embedments of the fibers in polyacrylic resins. The rate of water vapor transmission, measured as the diffusion constant, is larger for cotton than for rayon, wool, nylon, or Dacron. The respective diffusion constants are on the order of 134, 56, 39, 8 and 7×10^{-4} cm.^{2}/sec., under the relatively moist conditions of the tests, between 54 and 93% relative humidity.

While the possible influence of air in the lumen of cotton has not been completely evaluated, there is evidence that such influence has been reduced if not eliminated. However, this same evidence indicates that the cotton fibers were in part in an altered condition as a result of the embedment. Even so, the results suggest that cotton is a good choice of fiber for high water vapor transmission along the fiber.

Introduction

Information on the transmission of water vapor by textile fibers is desirable for better understanding of the problems of comfort, and as data for design in special applications such as upholstery, footwear, immersion suits and other protective clothing, and wrapping or packaging, where high resistance to liquid water is desired, combined with considerable permeability to water vapor.

Measurements of water vapor permeability of woven fabrics [4, 8] have indicated that in the lower ranges of fabric density, the main path of water vapor transfer is through the air spaces between fibers and yarns. This covers the densities characteristic of most apparel fabrics made from staple fibers, although filament yarn fabrics may be woven to higher densities in which the kind of fiber may be of more influence. In order to determine the role of the fiber itself in the passage of water vapor, it is necessary to account for the water vapor passage through air spaces in fabric structures, or to eliminate these air spaces. By embedding parallelized fibers in polymethyl and butyl methacrylate mixtures, it is possible to minimize the air spaces and at the same time have all the fibers oriented in the same direction, parallel to the path of water transfer. This procedure can also be applied to yarns.

Cotton differs from other fibers in having a central canal or lumen. The question of whether air remains in this lumen, or in the space between fibers in the tighter packing found in yarns, when embedded by the procedures used here, is considered in examining the results.

Goodings and co-workers [8] have also pointed out that an appreciable part of the resistance due to a layer of fabric is an "external resistance," that is, a resistance which is not proportional to the thickness. This external resistance is distinct from the resistance due to still air layers adjacent to the fabric, since it remains as a resistance associated with the fabric after the still air layers are accounted for. "The external-resistance component is conceived as arising when a diffusion flow undergoes a transition between two regions, one in which there is no obstruction, the other in which the flow cross section is restricted, in the body of a porous solid" [8]. A method for measuring the vapor transmission of fiber substance also should account for or minimize this flow restriction external resistance.

[1] A report of work done under contract with the U.S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. This contract is being supervised by the Southern Utilization Research Branch of the Agricultural Research Service.

This study covers two types of cotton, a coarse, thick-walled variety, Rowden, and a fine, thin-walled variety, Wilds. Both kinds are examined in the form of sliver, so that the fibers are relatively separate from each other. The Wilds variety is also examined in the form of yarn at two twists, 2.5 and 6.5 twist multiplier. Several other types of fiber were examined for comparison, using top or tufts of arranged fibers.

Method

Embedding

Measured and weighed lengths of sliver or bundles of yarn were placed in glass test tubes 12 × 72 mm. in external dimensions, and slightly over 10 mm. in internal diameter. The monomer mixture was in the proportion of 2 parts of methyl methacrylate to 8 parts of n-butyl methacrylate. Each monomer was extracted by washing in a separatory funnel with 20 parts of 5% sodium hydroxide, 20% sodium chloride solution, to remove inhibitor. Approximately 0.1% catalyst, benzoyl peroxide, was added to the mixture of washed monomers, and the mixture heated to 60° C. Before there was any large increase in viscosity, the warm mixture was poured on the fiber in the tubes, and thorough wetting obtained by squeezing from the side with glass stirring rods, followed by deaeration by the reduced pressure from a water jet aspirator. The embedments were allowed to harden at not over 60° for 2 hr. with further hardening at room temperature for 2 to 3 weeks. Higher temperatures in polymerization are to be avoided to prevent loss of volatile monomer and formation of bubbles.

Preparation of Sections

After cracking off the glass, the rods of polymer with embedded cotton were cut by a saw to $\frac{1}{8}$- to $\frac{1}{4}$-in. lengths in the portions in which the whole, undistorted sliver or yarn could be seen. These sections were made smooth and parallel sided by grinding against fine abrasive paper. The section was cemented to a brass rod by means of wax during the grinding, and the wax finally removed with Stoddard solvent. Each section was then tested for air channels by mounting it in a rubber tube so that air pressure could be applied by a rubber bulb of a medicine dropper. If bubbles could be observed coming through the section when the system was immersed in water, the section was discarded.

Measurement of Transmission

The smooth sections, from 1 to 5 mm. in thickness, were cemented with paraffin-beeswax mixture across the mouth of flat-bottomed cylindrical glass tubes, each 14 mm. high, 10 mm. outside diameter, approximately 8 mm. internal diameter. Each vial had been filled to a mark set 7 mm. below the top, with a saturated solution of ammonium dihydrogen phosphate, with excess crystals to assure saturation. These sealed vials were exposed inside a closed container (desiccator) containing dishes of saturated $Mg(NO_3)_2 \cdot 6H_2O$, with excess crystals. The whole system was kept in a constant temperature room at 21° C. The relative humidity in equilibrium with each salt solution at 21° C. is 93% inside, 54% outside, a difference of 39% [5]. Weighings at intervals of a week showed losses ranging upward from 1 mg. Steady rates were obtained after three weeks, and averages were taken over three or more weeks of steady state.

Analysis

In steady flow or diffusion of water vapor through a layer, the condition is analogous to the flow of electricity, being proportional to a potential, which in this case is the vapor concentration difference, and inversely proportional to a resistance, of which the largest part is the resistance of the layer of plastic and fiber. There is also resistance in the air layers inside the vial, and between the upper surface and the surface of the saturated salt solution, but if the resistance of the plastic and fiber portion is large, the air resistances can be neglected. In the same way, the external resistance due to flow restriction can be neglected to the extent that the total resistance is proportional to the length of path along the embedded fibers. The analog of Ohm's law is

$$\frac{Q}{At} = D\frac{(c_1 - c_2)}{L} \qquad (1)$$

where

Q = quantity of water transmitted, g.
A = cross-section area, cm.^{2}, of the actual path for water vapor
t = time, sec.
D = coefficient of diffusion, cm.^{2}/sec.
c_1, c_2 = vapor conc., g./cm.^{3}
L = path length, cm.

The coefficient of diffusion, D, is characteristic of the material of the system, in this case, the layer of plastic and fiber. Strictly speaking, c_1 and c_2 should refer to

the concentrations at the two surfaces of the layer of plastic and fiber, and an approximation is involved in using the concentrations in equilibrium with the salt solutions, since this leaves out of consideration both the resistance due to flow restriction and the resistance of air layers. The degree of uncertainty introduced by this approximation is discussed in presenting the results.

If we assume that the water vapor is carried by fiber alone, in proportion to M, the grams of fiber per cm.^{3}, then the cross section, A, can be defined as the average cross section of fibers across the embedment, and D becomes D_F, the coefficient of diffusion of water in the fiber material. From F, the grams of fiber per cm. length in the embedment, and M_F, the density of the fiber material,

$$A = \frac{F}{M_F} \tag{2}$$

Substituting in Equation 1, we have

$$D_F = \frac{QLM_F}{Ft(c_1 - c_2)} \tag{3}$$

The definition of A, the cross section, in terms of M_F, the density of the fiber material, involves the assumption that the fiber surface is everywhere in contact with the surrounding plastic, so that there are no air passages along the fibers. For cotton, it also involves the assumption that the lumen is filled with plastic. The further assumption, that every fiber extends from one side to the other, or that no fibers end within the section, is an approximation which is relatively good for all the section lengths used in this work, since these are much shorter than the staple length of the fibers.

In order to test the relationship between resistance to vapor passage and L, the path length in the section of plastic, one notes that resistance, R, is inversely proportional to the amount transmitted, Q; directly proportional to length of path, L; and inversely proportional to the amount of fiber, F, so that

$$R = K\frac{1}{Q} = K'\frac{L}{F} \tag{4}$$

This can be rearranged to show that F/Q, or F/W, where W is the rate of change in milligrams per week, should be proportional to L, the length of the embedment.

Results

Plastic Blanks

Sections of the polymerized plastic mixture, containing no fiber, but cast at the same time as the sections with fiber, have been mounted in the same way, as controls.

Some water vapor can diffuse through the polyacrylic ester itself, and through the wax seal. Assuming that all the water vapor which is lost, is lost through the plastic, we have D, the diffusion constant of water in the plastic, by Equation 1.

Results on the blanks are shown in Table I. The losses through one blank were high, which suggests a defect of sealing with the wax mixture. Repetition of the test after resealing this specimen gave results in line with the other blanks, indicating that the first sealing was faulty. This result also suggests that in any group of specimens, rates of diffusion which are higher than the general average should be given decreased weight, by taking the median rather than the average as the measure of central tendency.

TABLE I. Diffusion of Water Vapor through Polymerized Mixture of Methyl and Butyl Methacrylates

Specimen No.	L Path, cm.	W Rate, mg./week	D_p Diffusion constant, (cm.^{2}/sec.) $\times 10^{-4}$
B1	0.213	0.92	0.84
B2	0.172	0.97	0.71
B3	0.041	17.7	
Repeat		1.4	0.24
B4	0.125	0.85	0.62
B5	0.126	0.75	0.71

The losses through the other four blanks were low, and relatively independent of thickness of section. The internal diameter of the small glass tubes on which the sections were mounted is 0.83 cm., giving a cross section area of 0.54 cm.^{2}. The diffusion constant, calculated on this basis, is from 0.2 to 0.8 $\times$ 10^{-4} cm.^{2}/sec., which is a reasonable value for plastics of this type.

While one could apply a blank correction, the smallness of the blank in comparison with the diffusion constants calculated for sections with cotton fiber indicates that this is not necessary for the present experiments. The variability of the results, also, is large compared with the blank, which indicates that a blank correction would have little significance.

Results on Rowden and Wilds Cotton

Figures 1 and 2 show the relation between length of path through the plastic, and the function F/W, which is a measure of the resistance, corrected for the amount of cotton present. A generally linear trend is observed in each chart, and the slope and location are the same for Rowden cotton (Figure 1) and Wilds (Figure 2). This indicates that at least within the precision of the measuring method, there is no difference in vapor transmission for cottons of quite different wall thickness, since Rowden is a relatively coarse cotton, and Wilds a relatively fine cotton, with most of the commercial crop intermediate.

The measurements on Wilds yarn are similar to those on sliver, indicating an equal effectiveness of embedding, and no effect of variation in twist, in the range examined, on effectiveness of embedding.

Tables II and III show the diffusion coefficients, calculated by Equation 3. The range of each set makes it clear that there is little if any significant

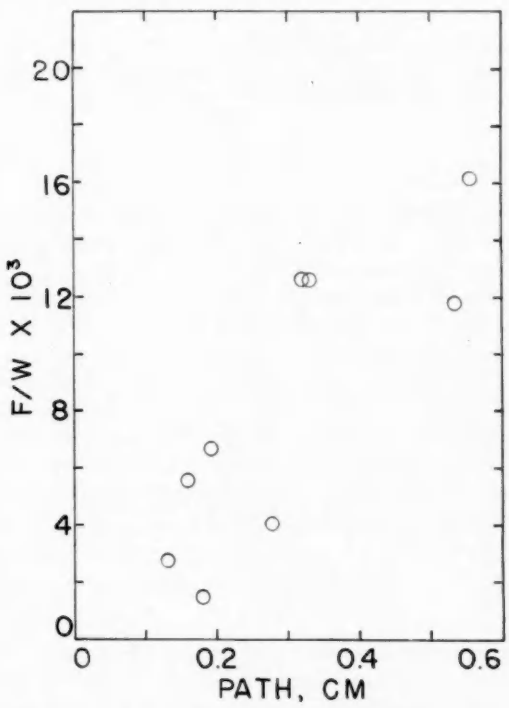

Fig. 1. Test of relation between length of path through cotton embedded in polymer and F/W, which is a measure of the resistance to passage of water vapor, adjusted for the amount of cotton. Data for Rowden cotton.

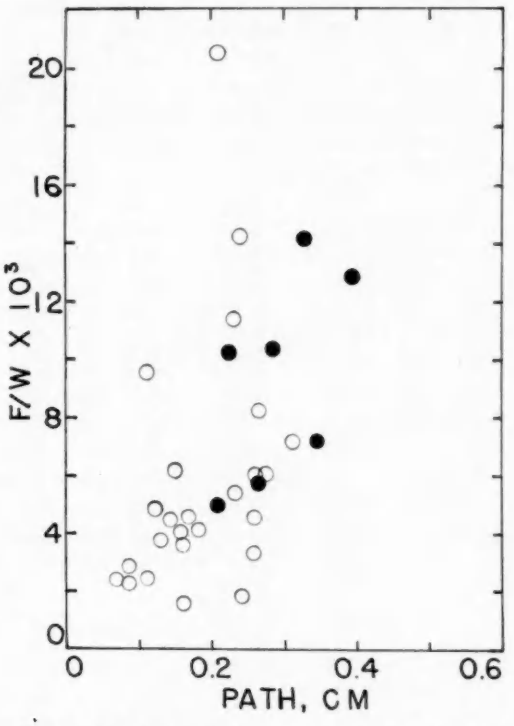

Fig. 2. Test of relation between length of path through cotton embedded in polymer and F/W, which is a measure of resistance to passage of water vapor, adjusted for the amount of cotton. Data for Wilds cotton. Filled circles represent yarn, open circles, sliver.

TABLE II. Diffusion of Water Vapor through Rowden Cotton, as Sliver, Embedded in Polymer

F Fiber amount, g./cm.	L Path, cm.	W Rate, mg./week	D_F Diffusion constant, (cm.²/sec.) $\times 10^{-4}$
0.0307	0.180	20.6	435
	0.556	1.9	124
	0.191	4.6	103
	0.534	2.6	163
	0.277	7.6	247
0.0334	0.158	6.0	102
	0.130	12.1	170
0.0328	0.330	2.6	94
	0.297	2.6	85
	Avg. of all 9:		169
	Avg. of lower 8:		136
	Median of all 9:		124
	Median of lower 8:		113

TABLE III. Diffusion of Water Vapor through Wilds Cotton Embedded in Polymer

Form	F Fiber amount, g./cm.	L Path, cm.	W Rate, mg./week	D_c Diffusion constant, (cm.²/sec.) $\times 10^{-4}$
Sliver	0.0565	0.130	15.0	124
		0.149	10.9	103
	0.0551	0.259	11.0	186
		0.086	24.2	136
	0.0471	0.181	11.5	159
		0.161	29.9	368
		0.112	19.1	164
	0.0546	0.258	11.9	202
		0.168	12.0	132
		0.086	19.2	109
	0.0601	0.264	7.3	116
		0.160	16.7	160
		0.068	25.0	102
	0.0651	0.257	19.4	276
		0.157	16.1	140
	0.0658	0.241	36.1	476
		0.143	14.8	116
	0.0607	0.310	8.5	156
		0.231	11.2	153
	0.0308	0.231	2.7	73
		0.208	1.5	36
	0.0343	0.239	2.4	60
		0.109	3.6	41
	0.0303	0.274	5.0	162
			Avg. of all 24:	156
			Avg. of lower 23:	142
			Median of all 24:	138
			Median of lower 23:	136
Yarn, 6's 2.5TM	0.0497	0.345	6.9	172
		0.284	4.8	99
Yarn, 6's 6.5TM	0.0655	0.208	13.2	151
		0.264	11.5	167
		0.224	6.4	79
	0.0735	0.394	5.7	110
		0.328	5.2	84
			Avg., all slivers and yarns:	149
			Median, all slivers and yarns:	136

difference between these values. If, in view of the results on the blanks, the one exceptionally high diffusion constant for each kind of cotton is omitted, the averages are brought closer together. The median of all the observations on both types of cotton, yarn and sliver, is $D_F = 134$. The corresponding grand average for observations on cotton is 154.

The results could be subjected to further statistical treatment, but it is believed that more real information would be obtained by anyone who repeated the experiments, with greater replication of conditions of embedding, and more attention to moisture relations, in the cotton and in the monomer mixture, during the embedding. This is suggested by the observations of Rollins and Tripp on this type of embedment, and by the fact that the four lowest values for Wilds sliver, in Table III, were obtained from two embedments which were prepared at a later time, along with the embedments of other types of fibers, the results of which are discussed later. The average of specimens of Wilds cotton is a diffusion coefficient of 52 and can be regarded as a lower limit for the estimate, from the present data, of the diffusion coefficient of water vapor in cotton.

The trend of the data in Figures 1 and 2, as L, the path through the plastic, approaches zero, is also toward zero, indicating that most of the resistance is indeed in the path provided by the cotton through the polymerized plastic. This indicates that the external resistance due to restriction of flow, plus that of external air layers, is small compared with the main resistance.

Resistance Relative to Air

Using the relation,

$$R = \frac{D_A L_M}{D_M} \tag{5}$$

in which R is the equivalent resistance in terms of centimeters of still air, D_A is the diffusion constant of water vapor in air (0.25 cm.²/sec.), D_M the diffusion constant in the material, and L_M the thickness of the material, we see that $(2.5 \times 10^{-1})/(134 \times 10^{-4})$ gives 19 as the ratio of resistance per unit thickness, if the pathway were pure cotton at 1.56 g./cm.³. Since the average amount of cotton per centimeter of embedment is 0.047 g./cm., and the cross section exposed is 0.54 cm.², the average concentration of cotton is 0.087 g./cm.³. The average length of section containing cotton was 0.23 cm., so

$$\frac{0.23 \times 1.56 \times 19}{0.087} = 78 \text{ cm.} \tag{6}$$

the average equivalent path in air. Since the maximum path in air within the system is on the order of 5 cm., this is additional evidence that the neglect of the air resistance, and calculating all the resistance as that of the cotton in the polymer, is justified, at the level of precision obtained in the present results.

Results of Low Humidity

After testing with 93% relative humidity on one side, 54% relative humidity on the other, as maintained by saturated solutions of $NH_4H_2PO_4$ and $Mg(NO_3)_2 \cdot 6H_2O$ respectively, some of the same sections were remounted with a desiccant, activated alumina, inside the vials. This resulted in operation between 54% and close to zero relative humidity.

The effect on vapor transmission was significant. Table IV shows that the amounts transferred, in milligrams per week, fell off to low values. One can see that the diffusion coefficients, were they to be calculated, would be much lower. Just what portion of the whole length of the cotton fiber is dried by the desiccant, and thus has this low permeability, is not known, although it could in principle be determined by study of the relations with whole path length and with similar studies at other, narrower ranges of relative humidity. Because this represents a bottleneck effect rather than the whole length of the fiber, no coefficients of diffusion have been calculated.

TABLE IV. Transmission through Cotton Fibers (Rowden Sliver) Embedded in Polymer Low Relative Humidity Range

F Amount of fiber, g./cm.	*L* Path, cm.	*W* Rate, mg./week
0.0307	0.180	0.7
	0.556	0.3
	0.191	0.6
	0.534	0.3
	0.277	0.5
0.0334	0.158	0.6
	0.130	1.1
0.0328	0.330	0.3
	0.297	0.4

This finding also suggests that the other coefficients are in a sense arbitrary; however, all measurements for which diffusion coefficients have been calculated are made under the same relatively moist conditions.

Possible Influence of Lumen

The low permeability at low relative humidity indicates that the resistance arises in the cellulose itself, rather than in an air passage through the lumen, or along the outside of the fiber.

Observation with the microscope of thin sections cut from the embedments indicated that in the fiber cross sections which showed large lumens, there was a plug of polymer. Hence, although it is not possible to be certain that the lumen of every fiber is filled with polymer, it seems likely that the measurements refer to cotton cellulose and not to a cotton-air system.[2]

Any air in the lumens would have two effects. The larger effect would be to increase the rate of diffusion, in a ratio of at least 19 to 1 (the ratio of diffusion coefficients), for the fraction of the cross section occupied by air. A smaller effect would be to reduce the density, M_c, used for the cotton, and hence reduce the calculated diffusion coefficient of water vapor in cotton, D_c. The range of uncertainty due to this factor is small since Wakeham's data [7] on the density of cotton surrounded by mercury, but with the lumen not filled, is 1.48. The lowest density reported for cotton in mercury, at low pressures, where the outer irregularities would also not be filled, is 1.30.

Comparison with Other Fibers

Tops, or fiber tufts of several other fibers, were mounted in polymerized plastic, exactly as with cotton. The results are shown in Table V. In calculating the diffusion coefficients for these fibers, the appropriate density for each fiber was used, in place of 1.56 used for cotton, substituting in Equation 4. The densities used are shown in Table VI. This table also shows the moisture regains of the fibers.

[2] After completion of these measurements, and reporting to the Cotton Chemical Finishing Conference, some of the cotton embedments were examined at the Southern Utilization Research Branch by Miss Mary L. Rollins and Mr. Verne Tripp (Letters of October 10 and November 7, 1956). Cross sections showed the lumen filled with plastic. However, it was also observed that significant numbers of the fibers had been expanded several fold in diameter, an effect of the acrylic monomer on wet cotton fibers. Longitudinal sections showed that this expansion extends for considerable distances (20 or more fiber diameters) along the length of a given fiber, but usually alternates with normal portions. This expansion of wet cotton has been noted by Rollins and Tripp in earlier work, in other connections. In the present case it may be the result of using room-condition cotton fiber, or the result of water which remains in the monomer mixture after the washing to remove inhibitor. The embeddings of viscose rayon did not show any signs of swelling in the filaments.

These observations suggest that the present measurements of diffusion constant of water vapor in cotton may not refer to cotton cellulose in a completely normal state, although they probably indicate the general order of magnitude of the diffusion constant for water in cellulose as compared with certain other fibers.

Some of the rates of transmission for fibers with low moisture regain are as low as or lower than the blanks of polymer with no fiber. Thus, calculation on the basis of transmission along the fiber, with no blank correction, results in apparent diffusion constants which must be larger than the values which would be obtained if this correction could be made. However, the results do indicate that the fibers with moisture regains above 5% do differ among themselves in apparent diffusion constant, and that the fibers with 5% regain or less are significantly lower, as a group, in diffusion constant.

As between cotton, nylon, and Dacron the expected relationship, that permeability should rank in order of moisture content, holds. However, both rayon and wool, with higher moisture contents, are outranked in permeability by cotton. There is some possibility that the higher diffusion coefficients for cotton may arise from the presence of air in the lumen of some of the embedded cotton fibers, or be influenced by the expanded diameters of segments of the fibers. Whether or not this is involved, the results do suggest a substantial advantage in water vapor transmitting capacity for cotton in comparison with fibers of low moisture sorbing capacity.

TABLE V. Diffusion of Water Vapor through Various Fibers Embedded in Polymer

Fiber	F Fiber amount, g./cm.	L Path, cm.	W Rate, mg./week	D_f Diffusion constant, (cm.²/sec.) $\times 10^{-4}$
Rayon	0.1005	0.119	14.4	61
Rayon	0.1005	0.127	12.4	56
Rayon	0.1005	0.220	7.6	59
Rayon	0.1094	0.187	7.9	48
Rayon	0.1094	0.227	33.9	253
Wool	0.0626	0.249	1.5	17
Wool	0.0626	0.185	5.1	45
Wool	0.0615	0.156	16.75	127
Wool	0.0720	0.231	4.1	39
Wool	0.0720	0.168	3.1	21
Nylon	0.0327	0.220	0.45	7
Nylon	0.0327	0.102	0.9	7
Nylon	0.0321	0.218	0.375	6
Nylon	0.0321	0.172	1.175	16
Nylon	0.0324	0.250	0.45	9
Nylon	0.0324	0.142	0.825	9
Dacron*	0.0588	0.290	0.35	5
Dacron	0.0588	0.145	0.55	4
Dacron	0.0582	0.224	0.725	8
Dacron	0.0582	0.228	0.6	7
Dacron	0.0541	0.191	1.325	14

* Du Pont polyester fiber

TABLE VI. Comparison of Moisture Regain and Water Vapor Permeability

Fiber	Commercial moisture regain [2], %	Density [1], g./cm.³	Diffusion constant (median), 10^{-4} cm.²/sec.
Wool	13	1.30	39
Rayon	11	1.50	56
Cotton	7	1.56	114
Nylon	4.5	1.14	8
Dacron*	0.4	1.38	7

* Du Pont polyester fiber

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The Application of Fluorochemicals to Cotton Fabrics to Obtain Oil and Water Repellent Surfaces[1]

Frederick J. Philips, Leon Segal, and Leopold Loeb[2]

Southern Regional Research Laboratory,[3] New Orleans, La.

Abstract

The application of some fluorocarbon compounds to cotton textiles to impart oleophobic and hydrophobic surface characteristics to the materials has been investigated.

Commercial and laboratory preparations of poly(fluoroalkyl esters of acrylic acid) and of chromium complexes of fluorine-containing monocarboxylic acids were used to treat cotton fabrics, thereby substituting low energy $-CF_3$ and $-CF_2-$ groups for the $-H$, the $-OH$, and $-CH_2OH$ of the cellulose surface of the cotton fibers. Data are presented to show the relative effectiveness of several classes of fluorocarbon compounds as satisfactory repellency treatments for cotton fabrics, and that modification of the cellulosic fabric surfaces by use of perfluorocarbon compounds considerably improves the resistance of the fabrics to wetting not only by water but also by organic liquids of low surface tension.

THE phenomena of the wetting of fabrics and their repellency to liquids have been studied heretofore primarily with water and aqueous solutions. A survey of recent literature has revealed little information on the wetting of fabrics by organic liquids. Zisman and co-workers [4, 6, 7, 8, 14] at the Naval Research Laboratory have studied the wetting of surfaces, and their most interesting results show that the wettability of a surface is directly dependent upon the chemical nature of the atoms populating the surface layer. They found that the least wettable surface is one having the lowest surface energy. Such a surface is composed of closely packed $-CF_3$ groups; increasing surface wettability was observed in the following sequence: $-CF_3$, $-CF_2-$, $-CH_3$, $-CH_2-$.

Wenzel [15] has considered the effect of surface roughness upon water repellency and concluded that the effect of roughness is to magnify the wetting properties of a solid. If a smooth surface has a positive tendency to wet, it will wet more readily when roughened; and if the smooth surface is repellent, the roughened surface will be more repellent.

Baxter and Cassie [2, 3] considered wetting of a porous surface with water from the standpoint of the geometry of an idealized yarn. Utilizing a grid made up of parallel cylindrical fibers of known radius, r, and an interfiber distance, $2d$, they were able to calculate the values for the real advancing angle of a drop of water on the surface in terms of the radius and interfiber distance, along with the areas of the solid-liquid interface and the liquid-air interface. With these values known, it was then possible also to calculate the apparent contact angle as a function of the fiber radius and interfiber distance. It was shown that both the apparent advancing and receding angles increase as the ratio $(r + d)/r$ is increased.

From the preceding, it can be understood that fabric geometry and surface roughness play a large part in determining the repellency of a fabric. However, by limiting the number of fabrics in any given study, surface roughness and geometrical factors can be controlled. With a given fabric of definite composition and construction, one must turn to suitable treating procedures for increasing repellency to liquids. According to the work of Zisman, the most satisfactory treatments would be those which modify the original

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[2] Present address: General Electric Corporation, Louisville, Ky.

[3] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

fiber surface to one of much lower energy. Stearic acid derivatives are often employed to render cellulose water repellent. Under ideal conditions these populate the surface with low energy $-CH_3$ groups. In the case of organic liquids of low surface tension one might anticipate that even lower energy surfaces would be required. The ideal fabric treatment in this case would be one which covers the fibers with close packed $-CF_3$ groups, or secondly, with $-CF_2-$ groups.

The above considerations together with the availability on a commercial scale of many fluorochemicals, particularly fluorocarbon derivatives of organic compounds, prompted interest in their application to cotton textiles. By substitution of the lower energy $-CF_3$, $-CF_2-$ groups for the original fiber surface, it was believed that properties other than hydrophobic surface characteristics could be obtained. Of the available fluorochemicals, the chromium coordination complexes of the saturated perfluoromonocarboxylic acids, $[CF_3(CF_2)_nCO_2Cr_2OH]^{4+}$, and the polymers of fluoroalkyl esters of acrylic acid,

$$(-CH_2CH_2-)_n$$
$$\quad\quad|$$
$$\quad COOCH_2R_f$$

where R_f is any perfluorinated alkyl group, seemed most suitable for application to cotton fabrics to obtain such surfaces. Reid [12, 13] has indicated that the perfluoro acid chromium complexes can be used to produce surfaces which are not only highly hydrophobic but also oleophobic; Ahlbrecht, Reid, and Husted [1] have suggested that the same properties can be obtained with the acrylic ester polymers.

The present paper describes the water- and oil-repellent cotton fabrics obtained by treatments with acid chromium complexes and with latices of the fluorinated esters of acrylic acid. In the case of the acid complexes, however, this investigation was broadened to include other fluorine-containing monocarboxylic acids that were capable of being complexed with chromium. These compounds included perhalogenated, fluorine-containing acids of the type, $Cl(CF_2CFCl)_nCF_2COOH$, and fluorinated monocarboxylic acids containing one hydrogen atom in the omega position, $HCF_2(CF_2)_nCOOH$.

Materials and Methods

The chromium complexes of the fluorinated acids listed below were prepared in the laboratory by reacting an isopropanol solution of the respective acids with a solution of a basic trivalent chromium salt. This salt was prepared from chromic oxide, isopropanol, and hydrochloric acid in the manner given by Goebel and Iler [9] for the preparation of hydrocarbon acid chromium complexes.

Although the above process is preferred for preparation of the complexes, they can be prepared alternatively by reacting chromyl chloride with the acids in an inert solvent (CCl_4) and in the presence of a reducing agent [12, 13]. In addition to the laboratory preparations a commercially available preparation of the chromium complex of perfluoro-octanoic acid was also obtained for this work. This material, under the trade name FC-804,* was furnished as a 30% solution of the complex in 95% isopropanol.

Although outside of two patents [12, 13], no literature was found which describes the fluorine-containing acid chromium complexes, a similar stearic acid chromium complex has been described in some detail both by Pavlin [11] and by Iler [10]. It is assumed that in the application of the chromium complexes of the fluorine-containing monocarboxylic acids to cellulosic materials the same mechanism holds as for the hydrocarbon acids.

The fluorine-containing acrylic polymers, employed in this work, were poly(1,1-dihydrotrifluoroethyl acrylate), abbreviated as PTEA, an emulsion polymer prepared for this laboratory by the Goodrich Research Center under the direction of Dr. Waldo Semon, and poly(1,1-dihydroperfluorobutyl acrylate), a latex commercially available as Poly FBA. The total solids content of PTEA was 16.5%, while that of the higher homolog, Poly FBA, was 35%.

The cotton fabrics employed included 8.5-oz. olive drab sateen, bleached 80 × 80 print cloth, and 80 × 80 print cloth in the grey state. The fabrics received no processing prior to use. Application of the fluoro-

* The mention of trade products does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

Perfluoroacetic acid
Perfluorobutyric acid
Perfluoro-octanoic acid
Perfluorodecanoic acid
3,5,6-Trichloro-octafluorohexanoic acid
3,5,7,8-Tetrachloroundecafluoro-octanoic acid
3,5,7,9,10-Pentachlorotetradecafluorodecanoic acid
5-H, Octafluoropentanoic acid
7-H, Dodecafluoroheptanoic acid
9-H, Hexadecafluorononanoic acid

chemicals to the fabrics was accomplished by simple padding and curing.

Treating solutions of the chrome complexes of the fluorine-containing acids were prepared on a weight/weight basis with proportions dependent upon the concentration of solid complex to be contained in the treating bath. The solutions were prepared by first diluting the concentrated complex solution with distilled water, then, with good stirring, slowly adding sufficient neutralizer to maintain the pH of the treating bath in the 4.0–4.5 range. Since a strongly acid solution of pH 2–3 is produced by hydrolysis of the complex on dilution, partial neutralization of the solution is required to minimize acid degradation of the cellulose during treatment. An aqueous solution of hexamethylenetetramine, HMTA, was used for this purpose. Addition of 10% aqueous HMTA, in a quantity equal to the weight of complex concentrate required for making up the treating solution to the desired concentration served to bring the solution into the above pH range.

In the present work an impregnation bath of 100 g. of solution was usually employed for each 16 sq. in. of fabric to be treated. The following is an example of the composition of a typical solution applied to a 4×4 in. swatch. In order to obtain 100 g. of solution containing 1.5% total complex solids from 30% FC-804, 5.0 g. of the complex concentrate would be diluted with 90.0 g. of distilled water and 5.0 g. of 10% HMTA. Fabric treatment consisted of a brief immersion (approximately 20 sec.) in the solution with no attempted control of wet pickup, followed by a 1-hr. cure at 110° C. After curing, the swatches were washed 10 sec. in a warm (40° C.), 0.05% solution of Igepal CO-630*, rinsed 10 sec. in running tap water and dried. Swatches of 8.5-oz. sateen were treated with solutions of the various complexes, ranging in concentration from 0.1% solids through 3.0% solids. The pH of these solutions ranged from 4.20 to 4.65. Swatches of the bleached and grey 80×80 fabrics were treated with solutions of FC-804 containing 0.1, 0.5, 1.0 and 2.0% solids; pH ranged from 4.15 to 4.33. The 80×80 fabrics were slightly tinted by these treatments with the diluted solutions of the green complex.

The fluorinated acrylic polymers were also applied to the fabric samples from aqueous dispersions. Impregnations were made with baths ranging in concentration from 1.0% total solids to the full strength emulsion. The fabric samples were treated by immersion into the treating solution until thoroughly wetted, after which the samples were air-dried 48 hr. before use. In place of air-drying, curing for 1 hr. at 150° C. was also employed. As with the fluoro-acid chrome complexes, impregnation baths of approximately 100 g. of solution were used for each 16 sq. in. of fabric to be treated. Dry pickup of the fabric samples was controlled by regulation of the polymer concentration of the bath along with regulation of the pressure on the squeeze rolls employed in padding.

For evaluation of the oleophobic properties of the treated fabrics, four test specimens of each textile, approximately 0.5×2 in., were placed on a rectangular piece of plate glass mounted above a mirror. Four drops of one of the common oils described below were placed on each of these specimens, with a different oil used on each one. Measurements were made of the time required for the droplets to disappear from the upper surface of the test specimen by either spreading on the surface of the fabric or penetration through the fabric.

The oils used for testing were USP white mineral oil, surface tension, γ, = 26.0 dynes/cm., at 27.3° C.; SAE #10 lubricating oil, γ, = 30.1 dynes/cm., at 26.8° C.; SAE #30 lubricating oil, γ, = 30.9 dynes/cm., at 25.8° C.; and unrefined peanut oil, γ, = 32.6 dynes/cm., at 25° C. The surface tensions of the test oils were measured with DuNouy Tensiometer at ambient room temperatures.

The test droplets were permitted to stand on the test specimens for a period of 336 hr. (14 days). If complete wetting had not occured at the end of this time, and if no penetration, i.e., no trace of liquid on the underside of the test specimen, took place, measurements on that particular sample were discontinued and the surface was considered to show excellent repellency to the test oil in question.

The hydrophobic properties of the treated materials were evaluated in the same manner—four drops of water were placed on each test specimen. The test specimen was then covered with a watch glass of such size as to cover the sample with the rim resting directly on the glass support plate. The purpose of the cover was to prevent rapid evaporation of the water drops, thus permitting an extended observation period (approximately 8 hr.) of the water repellency characteristics of each treated sample.

Evaluation of the physical properties of the treated fabrics included measurements of tear strength (Elmendorf), elongation, resistance to flat abrasion (Stoll

Abrader), air permeability (Permeometer), and water spray resistance (AATCC Spray Test). Portions of the cotton sateen treated with Poly FBA were also subjected to a series of mild launderings after which the materials were again evaluated for abrasion resistance, air permeability, and oil repellency. Conditions for laundering consisted of a 10-min. wash cycle in a small apartment-type washing machine using about 12 liters of a 0.1% tap water solution of Igepon T* at 60° C., followed by a 10-min. rinse in running tap water at 30° C. The samples were air-dried after rinsing. After air-drying the samples were ironed a total of 10 min. each, with an electric hand iron, 5 min. on each side. The surface of the iron was held at approximately 110° C., measured with a surface pyrometer. Three sets of samples—each set composed of three swatches (8 × 8 in.) with dry pickup of Poly FBA of 8.6, 14.0, and 26.2%, respectively, and an untreated control—were evaluated. Set #1 was evaluated after one laundering and ironing; Set #2 was subjected to two launderings and ironing treatments; and Set #3 to three.

Results and Discussion

Oil Repellency

Chromium Complexes

Excellent repellency to the test oils was observed where the sateen samples had been processed with solutions of FC-804 containing 1.5 to 2.0% complex solids; no penetration or wetting occurred with any of the four test oils placed on these fabrics (Table I). Only slight repellency to any of the test oils was observed at the lowest concentration, 0.1%, of complex solids employed in the treating bath. As the concentration of complex solids was increased, however, the repellency became progressively better until excellent repellency was obtained with the fabric treated with the 1.5% solution.

The laboratory preparations of the complexes of perfluoro-octanoic and perfluorodecanoic acids behaved, as would be expected, much the same as the FC-804. At the lower concentrations, 0.1 through 0.5% solids, little or no repellency was obtained. From concentrations of 0.7 to 2.0% solids, repellency

TABLE I. Time Required for Test Oils to Penetrate Treated Sateen

Sample treated with chromium complex of	% Complex solids in treating solution	Time, hr.			
		Mineral oil	SAE #10 oil	SAE #30 oil	Peanut oil
Untreated control	0	*NR*†	*NR*†	*NR*†	*NR*†
Perfluoro-octanoic acid	0.1	*NR*	*NR*	*NR*	*NR*
Perfluorodecanoic acid	0.1	0.02–0.05	0.03–0.05	0.07–0.13	0.12–0.32
Perfluoro-octanoic acid*	0.1	*NR*	*NR*	0.05–0.07	0.02–0.05
Perfluoro-octanoic acid	0.5	0.08–0.12	0.17–0.33	1.17–2.33	5– 24
Perfluorodecanoic acid	0.5	0.22–0.32	0.83–2.83	8–>336	96–312
Perfluoro-octanoic acid*	0.5	0.20–0.50	0.83– 72	72–144	72–120
Perfluoro-octanoic acid	0.7	0.13–0.20	0.42–1.42	2.33– 24	24–216
Perfluorodecanoic acid	0.7	0.50–0.66	2.33–3.83	8–168	192–>336
Perfluoro-octanoic acid*	0.7	0.75–2.50	72–168	72–>336	120– 336
Perfluoro-octanoic acid	1.0	0.66– 3	4– 24	96– 336	192– 336
Perfluorodecanoic acid	1.0	8–>336	8– 168	336–Indef.‡	336–Indef.‡
Perfluoro-octanoic acid*	1.0	2.25–>336	72–>336	312–>336	Indefinite
Perfluoro-octanoic acid	1.5	240–>336	>336–Indef.‡	Indefinite	Indefinite
Perfluorodecanoic acid	1.5	8–>336	312–Indef.	>336–Indef.	Indefinite
Perfluoro-octanoic acid*	1.5	Indefinite‡	Indefinite	Indefinite	Indefinite
Perfluoro-octanoic acid	2.0	>336	Indefinite	Indefinite	Indefinite
Perfluorodecanoic acid	2.0	>336–Indef.	168–Indef.	Indefinite	Indefinite
Perfluoro-octanoic acid*	2.0	Indefinite	Indefinite	Indefinite	Indefinite

* Commercial preparation of complex, FC-804.
† *NR* (no repellency)—drops wet completely in less than 1 min.
‡ Indefinite denotes no penetration or wetting of fabric by test droplets throughout test period.

improved progressively, but, contrary to observations with FC-804, some penetration of the fabric test specimens by the oil droplets occurred at the 1.5 and 2.0% solids concentrations. The data in Table I gives an indication of the effectiveness of these respective preparations applied from solutions containing 0.1 to 2.0% complex solids in preventing penetration by the oils. Untreated controls compared with these samples were completely and instantly wetted by the oils.

The wetting time ranges indicated in the table show the time in hours taken for complete wetting by the first drop and for complete wetting by the last drop of the test oil on each respective test specimen. In those cases where no penetration or wetting of the test specimens by the oil droplets occurred during the previously defined observation period of 336 hr. (14 days), the wetting time is classed "Indefinite." Where partial repellency resulted from the complex treatment, that is, the under surface of the test specimen was wetted by penetration without complete dissipation of the test liquid from the upper surface of the test specimen during the observation period, the wetting time is classed as being "greater than 336 hours."

Data for fabrics treated with solutions of the chromium complexes of perfluoroacetic and perfluorobutyric acids are not included in the table as these samples were wetted completely, almost instantly, by the four test oils, regardless of the concentrations of complex employed.

It can be deduced from the preceding that the chain length of the perfluoro-acid in the complex is an important factor. No repellency was obtained with the four-carbon acid, but good repellency was obtained with the eight-carbon acid. Because the perfluoro-acids lying between the four- and eight-carbon acids were not available, data were not obtained which could permit determining which chain length between the four- and eight-carbon chain would produce effective repellency. The apparent superiority of FC-804 to the laboratory preparations of the comparable complexes was attributed to unfavorable differences in the composition of the laboratory products. Reid [12, 13] has stated that chromium-to-acid mole ratios greater than 2.0 : 1 enhance the fluorocarbon character of the surface coatings prepared with the chromium complexes. Analysis of the commercial product, FC-804, indicated that it contained a ratio of 3.6 : 1. This suggested that the reduced repellencies of the laboratory preparations of the perfluoro-acid chromium complexes resulted from the lower chromium-to-acid ratio of 2.5 : 1, obtained by following the preparative procedure given by Goebel and Iler [9].

To test the above hypothesis, complexes of perfluoro-octanoic and perfluorodecanoic acids were prepared with chromium-to-acid ratios of 3.5 : 1, to 4.5 : 1, and 6.0 : 1. These products were applied to cotton sateen and tested as described previously. Extremely high repellency—no penetration or wetting—to the test oils was obtained on all samples treated with solutions containing 1.5% complex solids of each of the above preparations. Obviously then, to obtain satisfactory repellency on cotton fabrics, the

TABLE II. Time Required for Test Oils to Penetrate Print Cloth Treated with Different Concentrations of FC-804

Fabric	FC-804 Solids in bath, %	Time, hr.			
		Mineral oil	SAE #10 oil	SAE #30 oil	Peanut oil
Bleached	0	*NR**	*NR**	*NR**	*NR**
Grey	0	*NR*	*NR*	*NR*	*NR*
Bleached	0.1	*NR*	*NR*	*NR*	*NR*
Grey	0.1	*NR*	*NR*	*NR*	*NR*
Bleached	0.5	16	48	>336	>336
Grey	0.5	0.2	16	16–72	16–72
Bleached	1.0	>336	Indefinite†	Indefinite†	Indefinite†
Grey	1.0	>336	>336	>336	>336
Bleached	2.0	Indefinite†	Indefinite	Indefinite	Indefinite
Grey	2.0	Indefinite	Indefinite	Indefinite	Indefinite

* *NR* (no repellency)—drops wet completely in less than 1 min.
† Indefinite denotes no penetration or wetting of fabric by test droplets throughout test period.

complexes of the perfluoro-acids must have a chromium-to-acid ratio which is greater than 2.5 : 1.

Table II illustrates the effectiveness of FC-804 when applied to 80 × 80 print cloth. The better repellency of the bleached cloth over the grey at the intermediate concentrations of complex used can probably be explained in terms of the ease of wettability of the respective fabric samples. The bleached cloth undergoes a mild caustic scouring during the bleach process which helps considerably to increase the wettability of the fabric by removal of the wax present on the fibers. The increased wettability permits thorough wetting of the fabric samples as it passes through the treating bath, and this in turn results in good distribution and pickup of the treating chemical. With the wax present on the fibers—as is the case with the grey samples treated—wetting is hindered; hence, distribution and pickup, and possibly orientation, of the treating chemical by the fabric are also adversely affected.

The chromium complexes of the fluoro-chloro acids and the omega hydrogen, fluorine-containing acids (see *Materials and Methods* Section) failed to bestow oil repellency to the fabric regardless of the concentrations used. Variation of the chromium-to-acid ratio seemed to offer no improvement.

Poly(fluoroalkyl esters of acrylic acid)

For preliminary studies, samples of 8.5-oz. sateen were impregnated and processed as indicated in Tables III and IV. The samples of Table III were not padded after impregnation. Table IV presents data on samples which were padded to approximately 100% wet pickup after impregnation, followed by 48 hr. air-drying.

The results of the preliminary screening tests with the sateen samples, listed in Table III, indicated that Poly FBA is far superior to the lower acrylate, PTEA, as an oil repellent. In this series, the samples impregnated with Poly FBA were entirely repellent to SAE #10 oil, SAE #30 oil, and peanut oil at all the resin pickups shown. Penetration or wetting by mineral oil was withstood by Samples 4 and 5 throughout the observation period. Sample 2, however, required 20 to 72 hr. for complete wetting by this oil. The remaining sateen samples were not tested against mineral oil at this time. The samples impregnated with PTEA showed little resistance to the test oils. The best repellency was obtained with Samples 8 and 10 against SAE #30 oil. Some 72 and 48 hr., respectively, were required for wetting; only 3 hr. were required for complete wetting by peanut oil. The other two oils wet the PTEA-impregnated samples in a matter of minutes. It was also observed that Samples 9 and 11, both oven-dried, were wet quickly by all four of the oils.

The preceding results also indicate that air-drying or oven curing are equally effective processing means for Poly FBA impregnations. For the PTEA, air-drying seems to be superior to the oven cure.

TABLE III. Bath Concentration, Condition of Processing, Resin Pickup, and Time Required for Test Oils to Wet Cotton Sateen Impregnated with Poly FBA and PTEA

Sample	Total solids resin in treating bath, %	Processing			Dry pickup of resin, %	Wetting time, hr.			
		Method	Time, hr.	Temp.		Mineral oil	SAE #10 oil	SAE #30 oil	Peanut oil
					Impregnated with Poly FBA				
Control	0	—	—	—	0	*NR**	*NR**	*NR**	*NR**
1	1	Oven-dried	1	150° C.	2.7	—	Indefinite†	—	Indefinite†
2	2	Air-dried	48		2.7	20–72	Indefinite	Indefinite†	Indefinite
3	5	Oven-dried	1	150° C.	8.1	—	Indefinite	—	Indefinite
4	6	Air-dried	48		14.4	Indefinite†	Indefinite	Indefinite	Indefinite
5	8	Air-dried	48		16.1	Indefinite	Indefinite	Indefinite	Indefinite
6	20	Oven-dried	1	150° C.	28.2	—	Indefinite	Indefinite	Indefinite
7	35	Oven-dried	1	150° C.	69.3	—	Indefinite	—	Indefinite
					Impregnated with PTEA				
8	16.5	Air-dried	48		18.8	0.25	0.7–0.8	72.0	3.0
9	16.5	Oven-dried	1	150° C.	17.9	0.03	0.11	3.0	0.16–0.33
10	16.5	Air-dried	48		24.8	0.42	1.0–3.0	48.0	3.0
11	16.5	Oven-dried	1	150° C.	23.5	0.08	0.16–0.33	3.0	0.25–0.42

* *NR* (no repellency) drops wet completely in less than 1 min.

† Indefinite denotes no penetration or wetting of fabric by test droplets throughout test period.

TABLE IV. Bath Concentration, Resin Pickup, and Time Required for Test Oils to Wet Fabrics Impregnated with Poly FBA

Fabric	Total solids poly FBA in treating bath, %	Dry pickup poly FBA, %	Wetting time, hr.	
			Mineral oil	SAE #10, SAE #30, and Peanut oils
8.5-oz. sateen	0	0	*NR**	*NR**
80 × 80 print cloth (bleached)	0	0	*NR*	*NR*
8.5-oz. sateen	2	5.1	>336	Indefinite†
80 × 80 print cloth (bleached)	2	4.7	25–88	Indefinite
8.5-oz. sateen	5	8.6	Indefinite†	Indefinite
80 × 80 print cloth (bleached)	5	8.7	144	Indefinite
8.5-oz. sateen	10	14.0	Indefinite	Indefinite
80 × 80 print cloth (bleached)	10	14.3	>336	Indefinite
8.5-oz. sateen	20	26.2	Indefinite	Indefinite
80 × 80 print cloth (bleached)	20	29.4	Indefinite	Indefinite

* *NR* (no repellency) drops wet completely in less than 1 min.
† Indefinite denotes no penetration or wetting of fabric by test droplets throughout test period.

Further experiments with Poly FBA on sateen and 80 × 80 print cloth showed that it bestowed complete repellency to SAE #10 oil, SAE #30 oil, and peanut oil within the range of dry pickups studied (Table IV, and Figures 1, 2, and 3). Mineral oil penetrated the sateen sample with 5.1% dry pickup, but did not completely wet the sample throughout the 336-hr. observation period. At the higher pickup levels, the sateen samples showed excellent repellency to the mineral oil. The print cloth samples at the two lower dry pickups of polymer were wet completely by mineral oil in 25 to 88 and in 144 hr., respectively. With 14.3% dry pickup, the fabric was penetrated slightly but was not completely wetted by mineral oil during the observation period. Excellent repellency to the mineral oil was obtained at the 29.4% dry pickup level.

The better repellency to mineral oil of the sateen as compared with the print cloth at equivalent dry pickups of Poly FBA can probably be attributed to differences in fabric geometry of the two materials. This effect of fabric geometry, however, might be overcome with longer chain length in the perfluoroalkyl portion of the polymer. Longer chain length should also provide effective repellency against all of the test oils at lower dry pickups. Although such

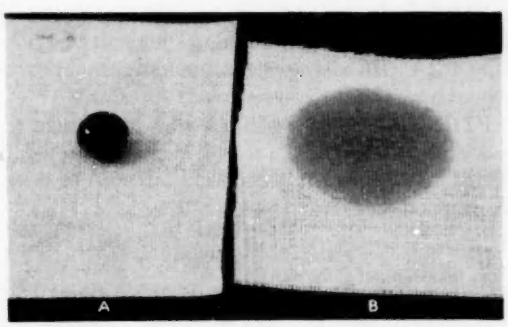

Fig. 1. Oil droplet (SAE No. 10 lubricating oil) placed on 80 × 80 print cloth. A. cloth treated with Poly FBA. B. untreated cloth.

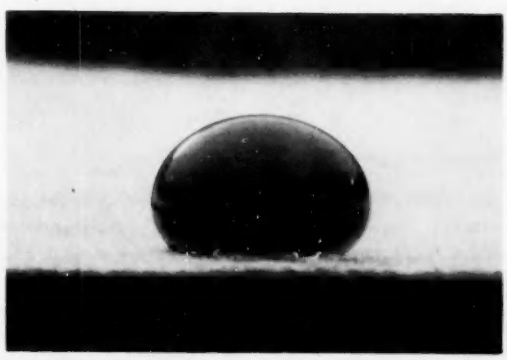

Fig. 2. A drop of SAE No. 10 lubricating oil on 80 × 80 print cloth treated with Poly FBA.

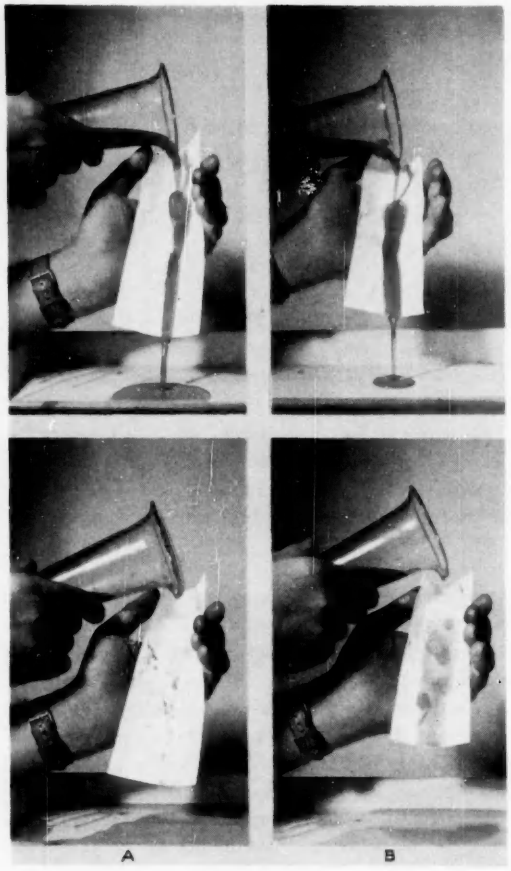

Fig. 3. Behavior of 80 × 80 print cloth with SAE No. 10 lubricating oil poured on. A. cloth treated with Poly FBA. B. untreated cloth.

polymers have been prepared [5], none higher than Poly FBA were available for this study.

Water Repellency

Chromium Complexes

Excellent water repellency was obtained for the materials treated with the commercial preparation of the chromium complex of perfluoro-octanoic acid, FC-804, and also with the laboratory preparations of the perfluoro-octanoic and perfluorodecanoic acid chrome complexes. In these instances, the water droplets failed to penetrate or wet any of the fabrics treated with solutions containing as low as 0.3% complex solids. Some water repellency was obtained for the samples treated with solutions containing the complexes of perfluoroacetic and perfluorobutyric acids, with the better repellency resulting for those samples treated with the four carbon acid complex.

TABLE V. Time Required for Water to Wet 8.5-oz. Sateen Treated with 0.5% Perfluoro-Acid Chrome Complexes

Sample treated with chromium complex of	Wetting time, hr.
Perfluoroacetic acid	0.25–0.5
Perfluorobutyric acid	3.5–>8.5
Perfluoro-octanoic acid	Indefinite*
Perfluoro-decanoic acid	Indefinite
Perfluoro-octanoic acid†	Indefinite

* Indefinite denotes no penetration or wetting of fabric by test droplets throughout observation period.
† Commercial preparation of complex, FC-804.

Table V gives a comparison of the water repellency of sateen samples treated with 0.5% solutions of the perfluoro-acid chromium complex preparations and illustrates the effect of increasing chain length on the repellency of the treated textile.

Swatches of sateen treated with 1.5% solutions of the fluoro-chloro acid complexes and the omega-hydrogen fluorine-containing acid complexes, with the exception of the sample treated with the 5-hydro-octafluoropentanoic acid complex, showed excellent repellency to the water drops. The sample treated with the five-carbon acid complex was wet completely in 2 to 8 hr. by the four test drops. No further study of the water repellency characteristics of these compounds at solution concentrations other than 1.5% was carried out at this time in view of their poor performance as oil repellents for cotton fabrics.

Poly(fluoroalkyl esters of acrylic acid)

Excellent water repellency was obtained at all dry pickups (Table III) of the fabrics impregnated with Poly FBA. In all cases the test droplets failed to penetrate or wet the respective test specimens.

PTEA exhibited little in the way of effective repellency; all samples (Table III) were completely wetted by the test droplets within 2 min. of being placed upon the fabric samples.

Physical Properties

Chromium Complexes

The tensile properties of the sateen treated with FC-804 were essentially unchanged from those of the untreated fabric. As can be seen in Table VI,

TABLE VI. Comparison of Physical Properties of Untreated Sateen and Sateen Treated with 1.5% FC-804

Property	Untreated fabric	Treated fabric
Elmendorf tear resistance, lb.	8.5	6.0
Grab breaking strength, lb.	146.6	146.0
Strip breaking strength, lb.	135.8	125.0
Elongation, %	14.6	14.7
Flat abrasion, cycles	425	363
Air permeability, ft.³/min./ft.²	13.8	12.3
Water resistance (AATCC spray test)	0	80

tear strength and abrasion resistance decreased somewhat (29 and 15%, respectively), but elongation and air permeability showed little or no change. Water spray resistance on the other hand increased strongly. The stiffness or feel of the treated fabric was, as well as could be discerned from comparative tests, no different from that of the untreated fabric.

Poly(fluoroalkyl esters of acrylic acid)

As shown in Table VII, the tensile properties of the Poly FBA-treated fabrics of Table IV also remain essentially unchanged from those of the untreated controls, except that with the 80 × 80 fabric a 30% increase was observed in elongation. Resistance to flat abrasion showed a marked increase with increasing dry pickup of polymer, while air permeability showed a decrease. Water spray resistance was again definitely improved. The stiffness of these Poly FBA-treated fabrics did not seem to differ much from that of the untreated controls.

Oil repellency and the physical properties of the samples subjected to the multiple laundering process were essentially unaffected by three cycles of wash treatments. All samples, with the exception of the sateen with 8.6% dry pickup, remained highly repellent to the test oils. Mineral oil penetrated the test specimens with 8.6% pickup after each laundering, but did not wet completely after 336 hr. on the fabric. These samples, however, were highly repellent to the other test oils after each wash treatment. Data given in Table VIII for the effects of the launderings on abrasion resistance and air permeability indicate that the improved abrasion resistance

TABLE VII. Physical Properties of Fabrics Impregnated with Poly FBA

Dry pickup poly FBA, %	Elmendorf tear resistance, lb.	Strip breaking strength, lb.	Elongation, %	Flat abrasion, cycles	Air permeability, ft.³/min./ft.²	Water spray resistance, AATCC spray test
			8.5-oz. Sateen			
Untreated Control	8.5	135.8	14.6	425	13.8	0
5.1	9.3	128.8	14.6	403	12.5	80
8.6	8.5	126.8	14.4	680	10.6	80
14.0	8.3	128.8	13.9	842	10.9	80
26.2	7.5	130.0	12.9	2091	11.1	70
			Bleached 80 × 80 Print Cloth			
Untreated Control	2.6	53.5	9.7	390	92.0	0
4.7	2.4	53.1	12.1	503	63.0	50
8.7	2.5	50.0	12.5	505	60.0	50
14.3	2.3	51.7	13.1	556	62.8	50
29.4	2.3	50.6	12.1	700	58.0	60

TABLE VIII. Effect of Laundering on Abrasion and Air Permeability of Sateen Impregnated with Poly FBA

Dry pickup poly FBA, %	Flat abrasion, cycles				Air permeability, ft.³/min./ft.²			
	Launder Number				Launder Number			
	Unlaundered	1	2	3	Unlaundered	1	2	3
Untreated Control	425	343	301	299	13.8	—	14.0	12.9
8.6	680	534	367	413	10.6	—	12.7	12.0
14.0	842	896	483	550	10.9	—	12.2	12.6
26.2	2091	1908	936	1034	11.1	—	10.5	11.9

is retained after three laundering cycles while the air permeability tends to approach that of the untreated fabric.

Conclusions

From the data presented it can be concluded (1) that treatment with the chromium complexes of perfluoromonocarboxylic acids such as perfluoro-octanoic acid chromic chloride and poly(fluoro-esters of acrylic acid) such as 1,1-dihydroperfluorobutyl acrylate (poly FBA) provides an excellent means of enhancing the repellency of cotton fabrics to oil and water and perhaps many other liquids; (2) that application of these chemicals to the fabrics is not complicated; and (3) that the utility of the treated fabrics is not impaired by the treatments since tear and breaking strengths, elongation, and air permeability are decreased only slightly, if at all, while flat abrasion resistance is greatly improved.

Acknowledgments

Appreciation is expressed to S. P. Koltun for the preparation of the chromium complexes used in this work, to R. L. Clayton for the surface tension measurements of the test oils, and to A. R. Markezich for the measurements of the physical properties of the fabrics. The omega-hydrofluoro acids were made available through the courtesy of Dr. J. W. Libby of the Du Pont Co.; the chlorofluoro acids by Dr. J. W. Copenhaver of the M. W. Kellogg Co.

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Molecular Organization in Keratins

Part I: Introductory Survey

R. D. B. Fraser and T. P. MacRae

Biochemistry Unit, Wool Textile Research Laboratory, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

Abstract

The present state of knowledge of the molecular organization and fine histological detail in keratins is reviewed. Methods of determining crystallinity are critically assessed, and the possible bearing of crystalline content on the occurrence of a structural unit in keratins is discussed.

Introduction

Since the discovery by Astbury and co-workers that the hard keratins of epidermal origin could be classified into two main types on the basis of their high angle X-ray diffraction patterns, considerable attention has been given to the elucidation of the stereochemical configurations of the polypeptide chain which characterize α- and feather keratin. Studies of the low angle X-ray diffraction patterns of various α-keratins by MacArthur [22] and by Bear and Rugo [6] show further that the similarities within the α-group extend to the organization of polypeptide chains at what is conveniently referred to as the macromolecular level.

Very little progress has been made in the interpretation of the low angle X-ray diffraction patterns of α-keratins or in the correlation of the principal spacings with the dimensions of histological components. The smallest structural unit so far recognized in electron microscope studies of degraded wool is the microfibril which is about 100Å in diameter and which, after certain drastic chemical treatments, appears as a linear aggregate of globules about 100–200Å in diameter [12, 18]. The low angle X-ray pattern provides evidence for an axial repeat of pattern at intervals of 195Å in human hair, but the uncertainty in the histological evidence precludes a quantitative comparison with the globular appearance of the microfibrils. A transverse spacing of about 90Å recorded by Bear and Rugo is probably related to the estimated width of a microfibril although the packing arrangement is not known.

Molecular Structure

There is now good evidence that the α-helix proposed by Pauling and Corey [28] substantially represents the polypeptide chain configuration that occurs in the crystallites of certain synthetic polypeptides. The close resemblance between certain features of the high angle X-ray diagrams obtained from poorly oriented synthetic polypeptides and many keratins suggests therefore that a modified form of the α-helix is the basis of the molecular structure of α-keratin [19].

A model of keratin structure consisting of hexagonally packed straight α-helices, such as occurs for example in crystallites of poly-L-alanine [4], can be excluded however due to its failure to account for the strong 5.18Å meridional reflection and also because the predicted density is much too low [2]. Further, it is difficult to see how such a structure could account for the very strong equatorial reflection corresponding to a Bragg spacing of 27Å.

In an attempt to formulate a more satisfactory structure, Crick [8] and Pauling and Corey [29] suggested independently that α-keratin contained groups of two or more α-helices so entwined that the axis of each helix formed a super-helix. The coiling of the α-helix was supposed by Crick [9] to result from side chain interaction while Pauling and Corey invoked the presence of repeating sequences of amino acids in the polypeptide chains. Although there is no evidence of such sequences at present, the model accounts broadly for many features of the high angle X-ray pattern such as the 5.18 meridional reflection,

the 27Å equatorial reflection, and the group of equatorial reflections at 9.8Å. The model suggested by Crick, although much less detailed and hence less readily tested, is the more plausible of the two in that the coiling follows logically from a consideration of side chain packing. It is doubtful however, if either structure can satisfactorily account for the observed density.

A single-coiled α-helix of the type envisaged by Crick, or Pauling and Corey would, assuming an average residue weight of 112 and a length of 195Å, corresponding to the axial repeat of pattern in hair, have a molecular weight of about 14,600. A triple helix of the type described by Crick would therefore have a molecular weight of about 44,000 in the same length. Recent determinations of the molecular weights of certain soluble wool derivatives give values around 48,000 [26], but the agreement may be fortuitous as there is, at present, no means of determining over what fraction or multiple of a fiber period each chain extends.

While the relatively high content of cystine has such a profound effect on the chemistry of keratins, its possible role in determining their molecular structure has received very little attention in the past, and recently Astbury has even suggested that it may be entirely absent from the crystalline regions [3]. However, Lindley and Rollett [21] using scale atomic models have shown that intramolecular disulphide bonds can exert a profound influence on both the sense and direction of an α-helix. Although their ideas have not yet been extended to a consideration of α-keratin structure, it is clear that they could provide alternatives to the coiled α-helix structures of Crick, and Pauling and Corey.

A further consideration relating to amino acid composition is that the relatively high proline content requires either relegation to the noncrystalline regions or special consideration for inclusion in the crystallites, since proline is known to produce considerable distortion of the α-helix.

Crystallinity

The models of α-keratin structure mentioned previously relate essentially to a crystalline phase, but there is abundant evidence that a considerable fraction of the wool fiber contains molecular chains which are not arranged in a regular fashion. The desire to relate the physical and chemical properties of wool to its molecular organization has led to the concept that a certain fraction of the fiber by weight, f_c, may be regarded as crystalline and the remainder, $(1-f_c)$, as noncrystalline.

Although the methods that have been used to estimate the crystalline fraction are all open to criticism, the convenience of the concept has been generally accepted. One of the principal difficulties of the concept, however, relates to the formulation of a satisfactory definition of f_c because of our ignorance of the structural organization in keratins.

The term crystalline implies a state in which there is complete three dimensional regularity of structure and there is evidence that in many polymers portions of a number of chains condense to form crystalline regions, as depicted in Figure 1a. Crystallinity of this type is characterized by a well-defined high angle X-ray diffraction pattern but no low angle pattern. In keratin, however, there is a wide variety of residues present in various proportions and the repeating sequence in a crystalline region will probably contain a large number of different residues. At all events any true crystallinity in keratins must necessarily be associated with very much larger repeating units, in at least one dimension, than in simpler polymers such as polythene, thus giving rise to a low angle X-ray diffraction pattern. The associated high angle pattern is likely, however, to be complicated by additional reflections from the types of organization discussed in succeeding sections.

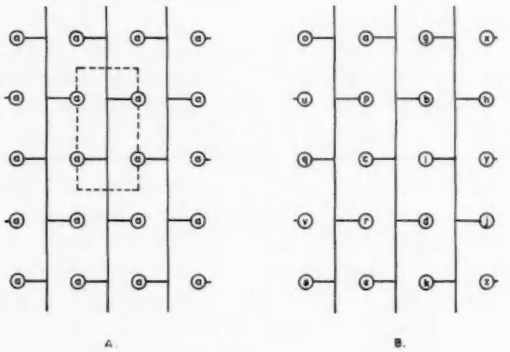

Fig. 1. Two dimensional representation of (A) crystallinity in a simple polymer and (B) related pseudocrystallinity in a protein. In (A) the symbol *a* represents a single chemical group and the repeat of pattern is shown by the dashed rectangle, there is no true repeat of pattern in (B) in the area shown; the various letters represent different amino acid residues.

Pseudo-Crystallinity

During the extension or regeneration of keratin fibers, it is easy to visualize the formation of oriented regions in which the main chains are arranged with three dimensional regularity and in this respect resemble the crystalline regions of simpler polymers. If, however, the distribution of side chains is not regular, as in Figure 1b, the region can only be regarded as pseudo-crystalline and will be characterized by a high angle X-ray diagram which is diffuse, quite apart from any effect of disorientation.

The high angle X-ray diagram of wool is such as to suggest that pseudo-crystalline regions may be present, but whether they should be included in the fraction f_c is open to question, as under some conditions they will behave as crystalline regions and others as noncrystalline.

Noncrystalline Regions

Although the remainder of the wool fiber is classified as noncrystalline, it must be borne in mind that a considerable degree of ordering may exist which would contribute appreciably to such properties as birefringence and infrared dichroism not normally associated with noncrystalline materials. For example, there will be regions in extended or regenerated fibers, if not in wool itself, where the polypeptide chains have a preferred orientation parallel to the fiber axis.

Determinations of Crystallinity

The regular three dimensional spacing in the crystalline regions of high polymers enables the lateral cohesive forces to exert a maximum co-operative effect so that in general these regions are not readily accessible to chemical reagents [23]. In contrast the noncrystalline regions are believed to contain a proportion of "empty space" which together with the irregular character of the lateral cohesive forces renders them considerably more accessible. The majority of the methods used to assess crystallinity are in fact attempts to measure the proportion of accessible material, the remainder being assumed crystalline.

Water Sorption

Provided that the crystalline regions of a polymer are relatively inaccessible to water, it follows that the amount of water sorbed at any particular relative humidity will depend on the crystalline content. The determination of the accessible fraction in wool from sorption data has been attempted both by analyzing the sorption isotherm [15, 25], and by correlating the number of water molecules sorbed with the number of chemical groupings that could act as sorption sites [33].

Sorption methods appear to be useful for assessing the relative crystallinities of different fiber types, but as an absolute method of determining f_c the following limitations must be recognized:

1. It is tacitly assumed that the distribution of potential sorption sites is uniform throughout the fiber. This is tantamount to assuming a uniform amino acid composition in both crystalline and noncrystalline regions, despite the fact that in silk, for example, they are known to be quite different [10].

2. It is assumed that the crystalline regions are completely inaccessible. In several polymers this assumption appears to be valid but in the case of wool there is evidence that water penetrates the crystallites to some extent [1, 22].

3. The noncrystalline regions may not be completely accessible. It is quite probable that pseudo-crystalline material, for example, is only partially accessible to water.

4. An error may arise from the fact that the polymer chains at the surface of the crystallites are free to absorb water [33]. Owing to the small diameter of the crystallites, ~ 100Å, [1, 31], the contribution of their surface to the total sorption may reach significant proportions.

5. The assumption, in the Hailwood-Horrobin analysis of the isotherm, that each residue is capable of combining with 1 mole of water. Some evidence of the inadequacy of this concept has been obtained from measurements on chemically modified wool [25].

Estimates of the crystalline fractions in a number of keratin fibers are collected in Table I, and it will be noted that the values given by the sorption stoichiometry method are only about half those given by analysis of the isotherm.

Deuterium Exchange

A very elegant method of estimating the degree of accessibility of keratins, devised by Speakman [32], depends upon a comparison of the degree of substitution of labile hydrogens achieved, by exposure to saturated deuterium oxide vapor, with the maximum possible degree calculated from the amino acid com-

TABLE I. Estimates of the Fraction of Crystalline Material (f_c) in Keratins

Material	Crystalline fraction	Method	Authors
Oxford Down wool	0.44	Sorption isotherm	Hailwood & Horrobin [15]
Romney wool	0.36	Sorption isotherm	Nicholls & Speakman [25]
	0.16	Deuterium exchange	Burley, Nicholls & Speakman [7]
Lincoln wool	0.30	Sorption isotherm	[25]
	0.13	Deuterium exchange	[7]
Merino wool	0.48	Sorption isotherm	[15]
	0.37	Sorption isotherm	[25]
	0.16	Deuterium exchange	[7]
Wool	0.15 to 0.18	Sorption stoichiometry	Valentine [33]
Hair	0.43	Sorption isotherm	[15]
Mohair	0.40	Sorption isotherm	[25]
	0.18	Deuterium exchange	[7]

position. The results obtained by Burley, Nicholls, and Speakman [7] are given in Table I, and they are seen to be in excellent agreement with the range of values obtained by the sorption stoichiometry method.

The values obtained by the deuterium exchange method are, however, as Speakman *et al.* have pointed out, dependant on the assumption that a uniform amino acid composition exists throughout the crystalline and noncrystalline regions. Recent infrared studies of the deuteration process indicate that complete exchange takes place in the side chain amide groups [13], thus casting doubts upon the validity of this assumption, although the results could equally be interpreted as being due to an exchange of the side chain amide groups in the crystalline regions. In either case the interpretation of the process is in question.

Another reservation which must be applied to Speakman's interpretation of the deuterium exchange reaction stems from the work of Linderstrøm-Lang [20] on the kinetics of this reaction in insulin. The results indicate that the stabilization effect of disulphide bonds can result in a very slow exchange of certain peptide hydrogen atoms, and it is possible that a similar effect occurs in the noncrystalline regions of wool.

Infrared Methods

The study of the infrared absorption spectra of polymers can provide two sources of information on crystallinity. First, it has been possible in a number of simple polymers to identify an absorption band which arises solely from the crystalline regions [24]. The optical density of this absorption in specimens of equal thickness should therefore, to a first approximation, be proportional to f_c and the method has in fact been applied in a number of cases. Although a crystalline absorption band has been tentatively identified in certain polypeptides [11], considerably more evidence of identification is required before it can be usefully applied to keratins.

A second source of information is provided by measuring the reduction of optical density that occurs in certain absorption bands associated with the peptide linkage after exposure to saturated deuterium oxide vapor [27] or immersion in liquid deuterium oxide [13]. Vibrations involving the N–H linkages of the polypeptide chains are considerably reduced in frequency when the hydrogen atom is replaced by deuterium and the residual absorption can be attributed to the nonaccessible linkages. The magnitude of the residual absorption is proportional to the number of unreplaceable peptide hydrogen atoms and therefore differs from the gravimetric method of Speakman discussed above, which estimates, in effect, the total number of inaccessible labile hydrogen atoms. The possible effect of disulphide linkages on the exchange of peptide hydrogen atoms in the noncrystalline regions, mentioned in the previous section, also applies to the infrared method.

Some of the difficulties encountered in the application of this method to keratins are discussed in reference [13].

Density

A comparison between the density of a polymer, measured in a nonswelling solvent, and that calculated from a model of the structure of its crystallites is a stringent criterion of its acceptability. If the observed density is greater than that calculated from the crystallite model, the structure is unacceptable. In fact the calculated density is always slightly higher than the observed density because polymers always contain a proportion of noncrystalline material in which the density is lower owing to the irregular packing.

Attempts to determine the crystalline fraction from the observed density, d, are based on the idealized assumption that a definite density d_a may be assigned to the noncrystalline regions and d_c to the crystalline regions. Using the fact that

$$\frac{1}{d} = \frac{f_c}{d_c} + \frac{1 - f_c}{d_a} \qquad \text{(i)}$$

whence

$$f_c = \frac{1/d_a - 1/d}{1/d_a - 1/d_c} \qquad \text{(ii)}$$

a value for the crystalline fraction is obtained.

Hermans [16] has used this relation to obtain the ratios of the noncrystalline contents of various celluloses by eliminating d_a from Equation (ii) and calculating d_c from the unit cell obtained by X-ray analysis. The possibility of applying a similar method to keratins will be discussed in detail in the second paper of this series.

X-ray Diffraction

Attempts have been made to deduce the crystalline content of certain polymers by comparing the relative integrated intensities of the discrete Bragg reflections from the crystallites and the background scattering from the noncrystalline regions [17]. The method can be applied, however, only when the crystallites exceed a certain minimum size and when estimates can be made of the specific scattering powers of crystalline and noncrystalline material. The difficulty of estimating the specific scattering powers has so far precluded the application of this method to keratins.

Other Methods

The degree of crystallinity in a polymer affects a number of other properties such as swelling, heat of wetting, ease of chemical and enzymatic hydrolysis, accessibility to reagents, extensibility, plasticity, and torsional rigidity, all of which may give information on the crystalline content. In the case of keratins, for example, le Roux and Speakman [30] demonstrated a correspondence between the crystalline contents of a number of wools as determined by the deuterium exchange reaction, and plasticity, sulphur content, and tyrosine content.

Summary

The complexity of the molecular organization in α-keratins is very great and the problems to be solved, as Kendrew [19] has pointed out, fall naturally into two classes. First the configuration of the polypeptide chain, about which a little is known, and second the disposition of these chains in the larger structural units, about which practically nothing is known.

In a keratin fiber such as wool, there is considerable evidence of heterogeneity at the histological level, but the available electron microscope studies on degraded fibers suggests that the microfibril constitutes a considerable fraction of the fiber weight. Taken together with the related equatorial low angle X-ray pattern, this evidence points to the microfibril as a unit of organization in the α-keratin structure. The meridional low angle X-ray pattern further suggests that the microfibril contains a repeat of pattern parallel to its length.

If the microfibrils are to be regarded as the crystalline component of α-keratins, the fact that they constitute a considerable fraction of the weight of a fiber might at first sight appear incompatible with the low values for estimates of crystallinity obtained by the sorption and deuterium exchange methods. However, they are not necessarily in conflict as it has been established that water penetrates the crystalline regions [22].

There is considerable evidence that while the polypeptide chain configuration in α-keratins is based on the α-helix, the arrangement of these chains is considerably different from that found in synthetic polypeptides in the α-form. The details of the organization of the polypeptide chains in the microfibrillar units of α-keratin must be regarded as virtually unknown although the structures proposed by Pauling and Corey [29], and Crick [8] indicate types of organization which can account for some of the observed X-ray reflections.

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Part II: The Densities of Native Keratins

Abstract

An apparatus for rapid density determinations is described in which small keratin samples may be dried and anhydrous solvent subsequently distilled onto them, the density being measured by finding the temperature at which the sample neither floats nor sinks. Densities of a representative series of keratins are reported and used to assess relative crystallinity. The measured densities are compared with those predicted by various models of α-keratin structure.

Introduction

In the preceding paper the use of density measurements for assessing crystallinity and for checking the correctness of models of the molecular structure of polymers was briefly discussed. In the present contribution the possibility of applying this method to problems of α-keratin structure is explored. Although reliable determinations of the density of wool have been made [7, 16], very little attention has been paid to other native keratins or to physically and chemically modified keratins.

The methods previously used with keratins require considerable quantities of material and are therefore unsuitable for measurements on structures such as porcupine quill tip. An apparatus in which the density of small samples could be measured with a precision of ± 0.001 was therefore devised and a representative selection of native keratin investigated. The results obtained with physically and chemically modified keratins will be presented in subsequent papers.

Experimental

Density values can be usefully employed to check model structures or assess crystallinity only if the sample is completely free from moisture and entrapped air and the immersion medium, assuming a displacement method is used, does not penetrate the noncrystalline regions. Hermans [6] has described an elegant flotation method, devised for measurements on cellulose, which satisfies these requirements, and a modified version of his apparatus was employed in the present work. In the flotation method, determinations are carried out by adjusting the temperature of a suitable solvent until the sample neither sinks nor floats, at which temperature the solvent and sample densities are equal.

The range of densities encountered in keratins precludes the use of a single solvent if the suspension temperature is to be confined to reasonable limits but a suitable range of immersion media was obtained by using mixtures of o-dichlorobenzene with either chlorobenzene or bromobenzene.

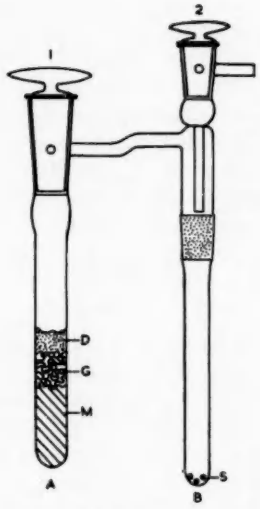

Fig. 1. Apparatus used for the determination of densities by the flotation method. *D*, desiccant (phosphorus pentoxide); *G*, glass wool; *M*, solvent mixture; *S*, specimens.

The apparatus employed is shown in Figure 1. A plug of glass wool was placed in limb A and the apparatus was dried in an oven at 100° C. Phosphorus pentoxide was then placed on the plug of glass wool and the immersion medium, previously dried with phosphorus pentoxide, was poured into limb A and tap 1 placed in position and closed. Three samples of the specimen were then placed in limb B and tap 2 placed in position and closed.

The contents of limb A were then degassed by freezing the immersion medium and evacuating the apparatus with a rotary oil pump. Tap 2 was then closed and the immersion medium allowed to thaw. This process was repeated until degassing was complete and then limb A was isolated by closing tap 1.

The samples were dried *in vacuo* for 3 hr. while limb B was maintained at 100° C. in a flask of boiling water having a condenser fitted to a side arm. Tap 2 was then closed and limb B immersed in a mixture of dry ice and trichloroethylene and tap 1 was opened. The immersion medium was then distilled over into limb B by placing limb A in a beaker of warm water (about 50° C.), the re-entrant tube in limb B effectively preventing condensation inside tap 2. When distillation was complete, tap 1 was closed and after the contents of tube B had thawed, dry air was admitted through tap 2. After closing tap 2, the apparatus was immersed in a water bath.

The temperature of the bath was then raised by steps of about 1° C. and the behavior of the specimens noted at each temperature. When all had sunk, a 10-ml. sample of the liquid in limb B was withdrawn after removing tap 2 and its density determined in a specific gravity bottle. From the measured coefficient of thermal expansion of the liquid and the suspension temperature of the samples, the densities could be calculated. It was found that a control of about ±0.01° C. was required in the water bath to eliminate convection currents in the liquid, and that temperature equilibrium was attained after about 20 min. at any particular temperature.

Results

The results obtained are given in Table Ia together with the temperatures of suspension. The values have been reduced to 25° C. by applying a small correction for the coefficient of thermal expansion of keratin. A value of 0.00016° $C.^{-1}$ was used for this coefficient, based on earlier studies of the variation of the density of wools and mohair with temperatures in the range 25–55° C. [16].

The range of values obtained in a single experiment did not in general exceed ±0.001 for fiber samples and ±0.002 for thin sections of hoof, horn, feather, and porcupine quill cortex. A considerable range of values was obtained, however, for porcupine quill tip, and this undoubtedly results from the variable amount of lower density cortex contained in the sample. The value quoted in Table Ia is the maximum so far obtained, but even this is probably less than the true density of the tip substance. The values obtained with echidna quill tip were less variable so that it might be concluded that the tip substance extends further down the quill than with porcupine.

In order to avoid as far as possible errors due to entrapped air, the hoof, horn, and feather samples were prepared in the form of 25μ sections and any medullated fibers in the mohair, human hair, and Lincoln wool samples removed following microscopical examination.

Density values for various keratins collected from the literature, are given in Table Ib, and it will be seen that the value for Merino wool in Table Ia agrees well with that given by King [7] but is somewhat lower than that obtained by Speakman, Scott, and Chang [16]. In the latter case drying was carried out at room temperature and the somewhat

TABLE Ia. The Densities of Certain Native Keratins Measured by the Flotation Method in Mixtures of o-dichlorobenzene with Chlorobenzene or Bromobenzene

Material	Density at 25° C. g.cm.$^{-3}$	Suspension temperature, ° C.	Mean residue weight, $\bar{M}$	Avg. volume per residue, Å^3
African porcupine quill (tip)	1.320	30	110*	138
African porcupine quill (cortex)	1.304	40	—	—
Echidna quill (tip)	1.335	29	110*	137
Feather rachis (goose)	1.269	46	101**	132
Horn (cow)	1.283	36	—	—
Horn (ram)	1.287	31	—	—
Hoof (cow)	1.288	47	—	—
Human hair (infant)	1.317	32	109‡	137
Mohair (Turkish, kid)	1.297	40	109†	140
Lincoln wool	1.299	37	—	—
Corriedale 56's wool	1.302	40	109	139
Merino 64's wool	1.302	41	112	143

* Assumed.
** Turkey feather rachis.
† Texas kid mohair.
‡ Adult hair.

TABLE Ib. Previous Values

Material	Density at 25° C. g.cm.$^{-3}$	Solvent	Method	Reference
Australian 80's wool	1.299	Benzene	Displacement	[7]
Lincoln 32–36's wool	1.290	Benzene	Displacement	[7]
Wool, 60's top	1.300	Benzene	Displacement	[7]
Wool, 60's top	1.302	Toluene	Displacement	[7]
Wool, 60's top	1.305	CCl_4	Displacement	[7]
Merino 60's wool	1.309	Benzene	Displacement	[16]
Corriedale wool	1.307	Benzene	Displacement	[16]
Mohair	1.304	Benzene	Displacement	[16]
Wool (fabric)	1.317	Xylene/CCl_4	Gradient column	[17]
Wool (unspecified)	1.30	Xylene/CCl_4	Gradient column	[12]
Porcupine quill	1.32	—	—	[11]
Keratins	1.29–1.305	—	—	[9]

higher value may be due to incomplete removal of water.

Discussion

In the preceding paper it was shown how the crystallinity of a polymer specimen could be related to its density by the expression

$$f_c = \frac{1/d_a - 1/d}{1/d_a - 1/d_c} \qquad \text{(i)}$$

assuming that the crystalline and noncrystalline fractions had uniform densities d_c and d_a respectively. If this expression is used to compare the crystallinities of α-keratins, it must be further assumed that d_c and d_a do not depend on mean residue weight. In order to test this assumption the average volume occupied by a residue, $\bar{v}$, in a number of α-synthetic polypeptides was calculated from the unit cells determined either by X-ray diffraction or molecular models, and the results are presented in Figure 2. The function $\bar{v} = a_0 + a_1\bar{M} + a_2\bar{M}^2$ was fitted in successive stages and the coefficients tested for significance. It was found that a_0 and a_2 were not significant and the value $a_1 = 1.3136 \pm 0.024$ was obtained by fitting $\bar{v} = a_1\bar{M}$. Since

$$\bar{v} = \frac{1.66\bar{M}}{d_c} \qquad \text{(ii)}$$

where $\bar{v}$ is measured in Å^3, the data suggests that d_c does not vary appreciably with mean residue weight. It must be emphasized that the variety of residues in the polypeptides for which information is at present available is insufficient for a thorough test of this assumption, and it is possible that the volumes per residue of other polypeptides may deviate

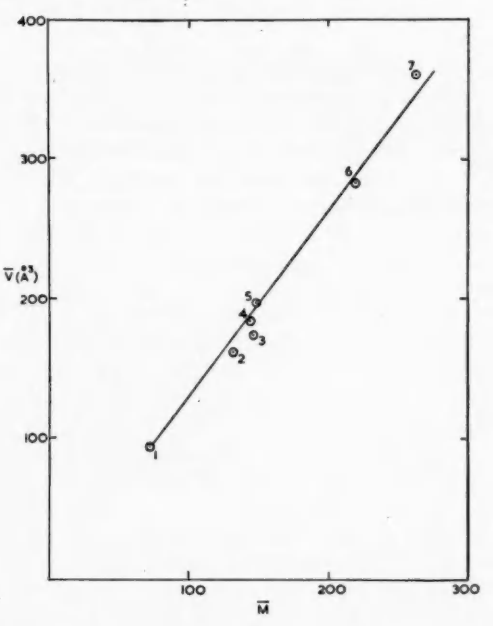

Fig. 2. The relation between average volume per residue ($\bar{v}$) in the crystalline state and mean residue weight ($\bar{M}$) of some synthetic polypeptides in the α-form. 1, poly-L-alanine; 2, 1:1 copolymer of DL-β-phenylalanine and L-leucine; 3, 1:1 copolymer of DL-β-phenylalanine and γ-methyl-L-glutamate; 4, poly-γ-methyl-L-glutamate; 5, poly-DL-β-phenylalanine; 6, poly-γ-benzyl-L-glutamate; 7, poly-ε-carbobenzoxy-L-lysine. The full curve is the fitted relation $\bar{v} = 1.314\bar{M}$.

significantly from this relationship. However, for the want of evidence to the contrary, it will be provisionally assumed that d_c does not vary appreciably with $\bar{M}$.

The evaluation of crystallinity from expression (i) requires a knowledge of both the crystalline and noncrystalline densities. In the case of cellulose [6] and a number of synthetic polymers the X-ray diffraction pattern can be indexed to give the dimensions of the unit cell and so d_c can be calculated from expression (ii). The value of d_a may be taken to be that of an isotropic sample of the polymer.

In the case of α-keratin no reliable unit cell has so far been determined and methods of preparing isotropic samples involve considerable chemical degradation. A reliable maximum value of d_c can be obtained from the specific volume calculated from the amino acid composition [10] which gives $d_c < 1.40$ g. cm.$^{-3}$.

Goodings [5] suggests from a consideration of the observed density of wool and the differences between observed and crystalline densities in silk and nylon that d_c lies between 1.37 and 1.50. He further suggested that the apparent density of wool in water, measured as 1.393 g.cm.$^{-3}$ by King [7] represents a minimum value for d_c. This latter suggestion must, however, be treated with considerable reserve as it is based on the assumption that the crystalline regions are not penetrated by water and that penetration of the noncrystalline regions is possibly incomplete. The former assumption is certainly incorrect [9].

It is clear that insufficient information is available at present for absolute values of f_c to be calculated from the observed densities of α-keratins. Purely for the purposes of comparison, we have assumed that $d_c = 1.39$, thus enabling Equation ii to be applied in the form

$$1 - f_c/1 - f'_c = \frac{1/d - 1/d_c}{1/d' - 1/d_c}$$

to give relative noncrystalline contents. These values are given in Table II and it is interesting to note that there is a qualitative correlation between the definition of the X-ray diagrams in, for example, hoof, wool, and quill tip and the relative contents of noncrystalline material.

TABLE II. The Relative Contents of Noncrystalline Material in Certain α-Keratins Assuming $d_c = 1.39$

Material	Density, g.cm.$^{-3}$	Relative noncrystalline content
Echidna quill tip	1.335	50
Porcupine quill tip	1.320	64
Human hair (infant)	1.317	67
Merino wool	1.302	81
Mohair (kid)	1.297	86
Hoof (cow)	1.288	95
Horn (cow)	1.283	100

The Molecular Structure of α-Keratin

It is generally accepted that a satisfactory model of the molecular structure of a polymer will lead to a calculated value of d_c which is greater than the observed density, usually by a factor of 1.05–1.10. In the case of α-keratin this test can be carried out by calculating the average volume occupied by a residue in the model structure and evaluating d_c from Equation ii, providing that the mean residue weight is known. Before discussing observed and calculated α-keratin densities, it is necessary therefore to consider the calculation of mean residue weight.

Mean Residue Weight

If 1 g. of dry keratin contains m types of amino acid residue and if the ith type, of residue weight M_i, contains n_i nitrogen atoms and contributes N_i g. of nitrogen, then the number of gram residues, g_i, of the ith type in 1 g. of dry keratin is

$$g_i = \frac{N_i}{14n_i} \qquad \text{(iii)}$$

and by definition the mean residue weight is

$$\bar{M} = \frac{1}{\sum_m g_i} = \frac{14}{\sum_m N_i/n_i} \qquad \text{(iv)}$$

The application of this expression to an amino acid analysis is only valid, however, when the nitrogen is completely recovered.

An alternative procedure, used by Astbury and Woods [2], is to use the relation

$$\bar{M} = \frac{\sum_m M_i N_i/n_i}{\sum_m N_i/n_i} \qquad \text{(v)}$$

which is readily shown to be identical with Equation

iv for a perfect analysis. If applied to an imperfect analysis in which say the mth amino acid is not recovered, the quantity evaluated becomes

$$\frac{\sum_{m-1} M_i N_i/n_i}{\sum_{m-1} N_i/n_i} = \frac{\bar{M}(1 - g_m M_m)}{1 - g_m \bar{M}} \qquad \text{(vi)}$$

since

$$\sum_{m-1} M_i N_i/n_i = 14 - M_m N_m/n_m$$

and

$$\sum_{m-1} N_i/n_i = \frac{14}{\bar{M}} - \frac{N_m}{n_n}$$

By setting $M_m = \bar{M}$ in Equation vi, it will be seen that the inherent assumption in this method is that the unrecovered amino acid has a residue weight equal to the mean.

A second method which has been used to calculate mean residue weights, due to Chibnall [3], requires a knowledge of the total nitrogen and values for arginine, histidine, lysine, tryptophane, and amide. If N is the total nitrogen less amide nitrogen, the expression may be written

$$\bar{M} = \frac{14}{N - \sum_m \frac{n_i - 1}{n_i} \cdot N_i} \qquad \text{(vii)}$$

which is identical with Equation iv for a perfect analysis. Since

$$\frac{n_i - 1}{n_i} = 0$$

except for the amino acids listed above, the inherent assumption is that all other residues in the sample contain only one nitrogen atom.

The values obtained by applying Equations v and vii to an amino acid analysis of Merino 64's wool is shown in Table IIIa. The results do not differ greatly, but the method due to Chiball has been adopted in the present work as a complete analysis of the specimen is not required and because the value obtained is not as dependent on the accuracy of amino acid estimation as that used by Astbury and Woods.

Mean residue weights for a number of keratins have been calculated from recent analyses and are presented in Table IIIa*. The range of values for

* It has been pointed out by a referee that somewhat higher values may be obtained by using weight or volume rather than number averages.

TABLE IIIa. Mean Residue Weights of Some Naturally Occurring Keratins Computed from Amino Acid Analyses

Material	Analytical data	Equation	$\bar{M}$
Merino 64's wool	Simmonds [14]	v	110
Merino 64's wool	Simmonds [14]	vii	114
Merino 64's wool	Simmonds [14]	vii	112*
Merino 64's wool	Corfield & Robson [4]	vii	112**
Merino 70's wool	Simmonds [14]	vii	111*
Corriedale 56's wool	Simmonds [14]	vii	109*
Texas kid mohair	Simmonds [15]	vii	109†
Angora mohair	Ward, Binkely & Snell [18]	vii	107†
Human hair	Simmonds [15]	vii	109†
Chicken feathers	Ward, Binkley & Snell [18]	vii	105†
Turkey feather rachis	Schroeder & Kay [13]	vii	101†

* Using Leach's figure for amide N [8].

** Using Simmonds value for the total nitrogen of Merino 64's wool [14].

† Assuming no tryptophane present.

TABLE IIIb. Values Calculated by Ward and Lundgren [19] from Earlier Composite Data

Material	Equation	$\bar{M}$ range
Wool	v	108
Wool	vii	114
Hair	v	107–108
Hair	vii	118–112
Horn	v	104–107
Horn	vii	120–112
Porcupine quill	v	112
Porcupine quill	vii	113–114
Feather	v	101–103
Feather	vii	116–107

α-keratins (107–112) is remarkably small while the feather keratin values appear to be significantly lower. Where possible, average volumes per residue $\bar{v}$ have been calculated from this information and the observed density and are recorded in Table Ia.

The α-Helix

From the data on α-synthetic polypeptides collected in Figure 2, the densities included within the 95% confidence limits are $d_c = 1.21$ to 1.32 g.cm.$^{-3}$ When these are compared with the observed values, it must be concluded that the packing arrangement of the residues in α-keratin is somewhat more compact than is general in structures based on straight α-helices containing 18 residues in 5 turns. This conclusion is supported by the fact that the prominent 9.8Å equatorial reflection in the X-ray diagram

TABLE IV. A Comparison of the Observed Density of Merino Wool with Model Structures

Structure	Average volume per residue ø Å³	Density ($\bar{M}$=112), g.cm.⁻³
Merino wool	143	1.30
α-Helix (3.6 res./turn), hexagonal packing a_0 = 11.3Å	166	1.12
Coiled-coil model (Pauling & Corey), a_0 = 32.4Å	151	1.23
Synthetic polypeptide structures (α-form)	141 to 154	1.21 to 1.32

of α-keratin, if indexed as the $10\bar{1}0$ reflection of a hexagonal unit, gives an average volume per residue of 166Å³. With a mean residue weight of 112, this leads to a predicted value d_c = 1.12 g.cm.⁻³ which is obviously too low [1].

It is clear that from density considerations as well as the X-ray evidence considered in Part I, a simple system of hexagonally close packed α-helices is not an adequate model for α-keratin.

The Coiled-Coil Model

In an attempt to give better agreement between observed and predicted X-ray reflections, Pauling and Corey [11] proposed the modified α-helix structure described in Part I. The average volume per residue predicted by this model is 151Å³ which is significantly greater than the value given in Table Ia for Merino wool which was calculated from the observed density and the mean residue weight. Applied to wool therefore, the structure does not satisfy the simple test customarily applied to polymer models in that it is not sufficiently compact to give a predicted density greater than that observed.

It could be argued that the structure of porcupine quill tip, for which the coiled-coil model was suggested is substantially different from that of wool, but the X-ray pattern of wool is sufficiently similar to that of quill tip to render this improbable. Alternatively it might be supposed that the density in the noncrystalline regions was greater than in the crystalline regions due to a preponderance of residues with low specific volumes. However, there is no unequivocal chemical evidence to support this view and the observed density difference between quill tip and horn is the reverse of what might be expected from this supposition.

A possible explanation, which cannot be entirely excluded, is that the mean residue weight in the crystalline regions of wool or quill tip exceeds the range of values given in Table IIIa. For example, a value of $\bar{M}$ = 120 in the coiled-coil model would give a predicted density of 1.32g.cm.⁻³. as observed for quill tip. However, the crystalline density might be expected to be somewhat greater than the observed density thus requiring $\bar{M} > 120$, *e.g.*, for d_c = 1.39 a value of $\bar{M}$ = 126 would be required.

The great virtue of the coiled model is that the 1.49 and 5.18Å meridional reflections and the '9.8' and 27 Å equatorial reflections in the α-keratin X-ray diagram are satisfactorily predicted but some modification may be necessary, in view of the discrepancies discussed above, to increase the predicted density.

Acknowledgments

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A Laboratory Apparatus for Chemical Modification of Cotton Yarn

Norton A. Cashen, Edmund M. Buras, Jr., and A. Mason DuPré, Jr.

Southern Regional Research Laboratory,[1] New Orleans, La.

VARIOUS methods have been reported for the practical handling of cotton textile materials for dyeing, finishing, and chemical modification with retention of the fibrous or textile form. For treatments in which toxic, irritating, or otherwise noxious materials are being handled, attention has been given to the use of closed-system equipment, such as package and beam dyeing equipment [3], enclosed standard equipment such as dye becks [2], and the development of continuous ranges which are hooded or enclosed as far as practical limitations will allow [4, 6].

The development of laboratory-scale apparatus for continuous processing in closed or nearly closed systems appears to have received less attention, however. One such apparatus, which is compact and relatively simple in construction, has been used in this laboratory for the chemical modification of cotton yarn employing irritating and noxious chemicals. As will be seen, it is based on the use of molten metals for heat transfer, and as a sealant between chambers within the apparatus. The use of molten alloys for heat transfer has received prior attention for high temperature dyeing, both in the laboratory and in the plant, i.e. the Standfast Process [7]. For experiments on a laboratory scale, at least, we have found that liquid mercury may be used effectively at lower temperatures for heat transfer from exothermic reactions which occur in some chemical modifications of cotton cellulose. In the application for which originally intended, namely partial acetylation of cotton yarns, the apparatus to be described has made possible continuous processing of yarn with very close control of time and temperature of the impregnation bath, independent of the temperature of the heat exchange medium in the reaction column. Apparatus of this design has also been useful in the continuous cyanoethylation of cotton yarn [5].

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

Description of Apparatus

The apparatus, as illustrated (Figure 1), may be used to carry out three phases of the process—impregnation, reaction or curing, and washing—in one unit on a laboratory scale.

1. *The impregnation chamber* (Figure 1-1) consists of a glass tube, 3.5 cm. in diameter, and extending 25 cm. downward, terminating slightly below the surface of the liquid metal, which confines the impregnating bath to this part of the apparatus. The upper rim of this tube is fused to the glass outer wall which jackets the impregnation chamber containing the reagents. Water, which is circulated in this jacket to cool the reagent solution, also serves to wash the treated yarn as it emerges from the reaction column. By using such a chamber, the impregnation bath is contained in a nearly closed vessel with a small yarn entrance port, thereby minimizing the escape of vapors to the atmosphere. In addition, the use of small volumes of liquid facilitates close control of temperature and composition of the bath. Furthermore, the temperature is independently controlled from that of the medium in the reaction tube. In some applications, advantage may be taken of this in the re-

duction of impregnation temperature while time of immersion is increased, so that heavy yarn constructions can be completely and uniformly impregnated with the reagent before any reaction takes place.

If the apparatus is to be used to study a continuous rather than a batch process, the period of impregnation may be controlled by changing the volume and consequently the level of the impregnation bath, thereby changing the duration of immersion independently of the rate of travel through the reaction column.

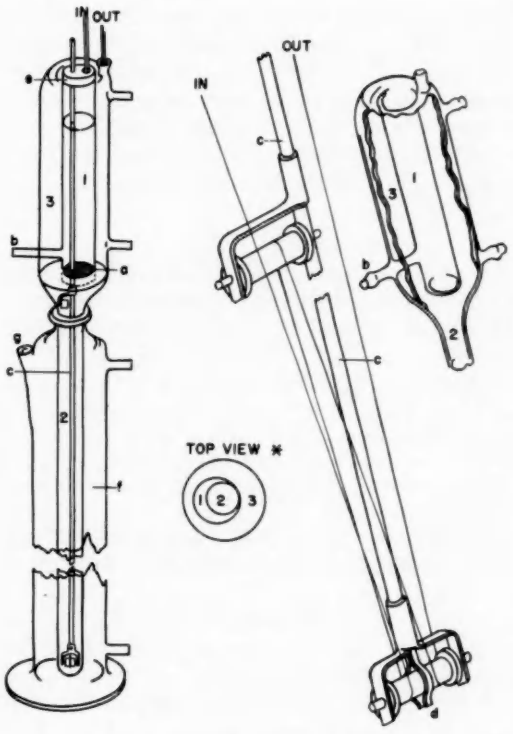

Fig. I. Laboratory apparatus for chemically treating cotton yarn. (1) Impregnation chamber. (2) Reaction column. (3) Wash chamber. (a) Mercury-impregnation bath interface. Liquid metal creates a seal between the impregnation and wash-bath. (b) Impregnation-bath entrance and drain port—permits "chicken feeder" system for maintaining constant volume. (c) Yarn routing system—stainless steel rod and pulleys. (d) Pulley divider—lower pulley accommodates two passes of yarn. (e) Rubber stopper. (f) Jacket for temperature control—for regulating temperature of metal reaction column. (g) Thermometer socket.

* The top view shows the offset arrangement of the separate compartments which is required to permit entry of the pulleys to the reaction column.

2. *The reaction column* (Figure I-2) contains the molten metal which is the most dense component of the liquid system. It is constructed of 3 cm. O.D. Pyrex glass tubing, and 45 cm. long. Many liquid metals may be used, depending on the nature of the chemicals and the temperature range of the process employed. In partial acetylations, mercury has been found suitable.

Within the mercury column is a stainless steel pulley system (Figure I-c), firmly held in place by a rubber stopper seated into the top of the apparatus. Through the use of an upper and lower pulley, 2 m. of yarn are immersed in a bath about 0.5 m. in depth. However, the dimensions are arbitrary, being limited by the quantities of the material to be handled, and the inside diameter of the Pyrex tube in which it is contained. An apparatus of the dimensions given easily accommodates a draw of ten strands of 12/3 cotton yarn.

For temperature control of the heat transfer medium, the column is jacketed with a circulating water bath (Figure I-f) which can be adjusted to a desired temperature. The position of the upper pulley should be sufficiently below the interface (Figure I-a) of the impregnation bath and liquid metal, keeping the yarn away from a temperature gradient zone. If other heating requirements are to be met, it may be that an electrical heating mantle can be used in place of the water bath system.

A thermometer is inserted through a standard taper joint (Figure I-g) into the stream of the bath, and serves to indicate the processing temperature.

3. *The wash chamber* (Figure I-3) contains circulating water (the same which regulates temperature of the impregnation bath) which serves to wash the processed yarn as it emerges from the reaction column and passes through this chamber. In using the apparatus for partial acetylation, the water also serves to terminate the esterification reaction.

Operation

The operational procedure for use of the apparatus in the chemical modification of yarn may be simply outlined:

a. Load reaction column with a suitable liquid metal. A sufficient volume must be added in order to produce a seal (Figure I-a) between the impregnation and wash chambers.

b. Route the yarns over the pulleys (Figure I-c) and lower into the reaction column.

c. Adjust reaction column temperature.

d. Circulate cold water bath through the impregnation chamber jacket.

e. Add impregnation bath.

f. Draw yarns through to fully load the reaction chamber under controlled temperature.

Discussion

The use of an apparatus of the type described affords numerous advantages, some of which are as follows:

a. A minimum quantity of reagents is required.

b. The escape of irritating and noxious vapors is minimized when such chemicals are employed in processing cotton yarn.

c. Good heat transfer is obtained. Large quantities of diluent for heat absorption are no longer needed, if reaction is exothermic.

d. A relatively low liquid carry out is obtained without the use of squeeze rolls, with their possible flattening effects on the yarn.

e. Transfer of material from the impregnation bath to reaction column is accomplished without exposure to air. This should minimize the possibility of air oxidation, such as might occur in the treatment of cotton under alkaline conditions.

f. Direct transfer from impregnation bath to a good heat transfer medium, and from reaction system to wash. There are no periods of uncertain timing or temperature.

g. The reaction is carried out in a uniform thermal field, so that migration, brought about by local overheating in the fiber, is minimized.

h. Yarn is processed under pressure and with slight tension, thus minimizing difficulties associated with shrinkage and kinking of yarns.

i. Either batchwise or continuous operations may be simulated.

The most apparent disadvantages of a process involving the use of liquid metals are that the chemical systems employed are limited to those which are not reactive with available metals, and that a small amount of metal is carried off with material being processed.

Having noted the forementioned advantages, it is suggested that an apparatus as described, employing a liquid metal as both heat exchange medium and sealant between chambers, may be used advantageously in the investigation of the following types of textile processes:

1. Chemical processes involving exothermic reactions between fiber and reactant, which may produce local overheating within the fiber, resulting in nonuniformity of reaction, and local degradation of the material being processed.

2. Curing processes, such as those involving resin polymerizations [1]. An apparent time lag in the initiation of polymerization occurs upon entering the oven, since ovens commonly in use do not possess good heat transfer characteristics, and the time taken to dry and raise the temperature to that required for reaction is quite considerable, and difficult to control [8]. Rapid heat transfer at this stage is desirable, because migration of the resin commences and is stopped only by the onset of polymerization.

3. Treatments involving alkaline solutions which may promote air oxidation of the cotton.

Summary

A laboratory apparatus for the chemical processing of cotton yarn, which utilizes the excellent heat transfer characteristics of liquid metals to control temperature and minimize problems of local overheating in exothermic reactions, is described. Advantages are cited, principal of which is excellent control of temperature and time of treatment.

Acknowledgment

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The Interpretation of Creep Failure in Textile Fibers as a Rate Process

Bernard D. Coleman and Andrew G. Knox

E. I. du Pont de Nemours and Company, Carothers Research Laboratory, Wilmington, Del.

Abstract

Some theoretical results are presented which have been obtained using an absolute reaction rate approach for discussing the time dependence of creep failure in textile fibers. The methods used permit a calculation of the functional form of the following relationships: (1) the dependence of the time required for breaking on the magnitude of a sustained dead load; (2) the dependence of the fatigue life under a noncompressive periodic load on the stress amplitude and frequency; (3) the dependence of the tensile strength on the rate of loading used in its measurement; (4) the dependence of the strength loss in a fatigue experiment on the time of exposure. The theory suggests that it may often be possible to predict the results of measurements of all of these quantities from the measurement of one of them. The conditions under which this is true are discussed in detail here.

Introduction

This paper is concerned with the creep failure, under time-dependent tensile loads, of partially oriented polymeric filaments of such materials as drawn nylon, drawn Dacron[1] polyester fiber, rayon, and cotton.

In a previous article [2] a simplified model was presented for the calculation of the time, t_B, required for the breaking of a filament which has been subjected to a uniaxial loading history, $f(t)$. The development of the model was based on the concepts of the theory of absolute reaction rates as developed by Eyring [4], and applied to viscoelastic phenomena by Tobolsky et al. [9, 10]. The purpose of the present discussion is threefold: to review some of the principal results which have been obtained with this model, to present some new results, and to emphasize certain limitations.

Theory

The proposed theory regards the rate-determining step in the mechanical breakdown of a load-bearing fiber as being the displacement of a set of entities called force centers. It is assumed that the displacement of the force centers is a thermally activated rate process. The mean relative displacement at a time, t, is measured by a quantity, γ, which has the dimension of length, and is defined to be zero at the moment that the fiber is first loaded. It is further assumed that there exists a critical value of γ, called γ_B, such that when $\gamma = \gamma_B$ at the weakest cross section of the fiber, the average force center in this cross section finds itself outside of the field of force of its neighbors and is then unable to support the applied load. From the moment that γ reaches γ_B onward, the breakdown process proceeds with catastrophic rapidity, and, therefore, the time required for γ to reach γ_B may be regarded as determining t_B.

The rate of increase of γ is governed by the differential equation [2]

$$\frac{d\gamma}{dt} = \frac{2\lambda kT}{h} \exp\left\{\frac{-\Delta F^{\ddagger}}{RT}\right\} \sinh\left\{\frac{f(t)\delta}{2kT}\right\} \quad (1a)$$

where $\Delta F^{\ddagger}$ is the free energy of activation for a jump along the fiber axis, λ (jump distance) is the separation between the positions of minimum potential of mean force, δ (displacement volume) is equal to the product of the effective cross-sectional area per force center and the jump distance, T is the absolute temperature, R is the gas constant, k is Boltzmann's constant, and h is Plank's constant. To find t_B for a particular $f(t)$, one integrates Equation 1a subject to the conditions:

$$\text{at} \qquad t = 0, \qquad \gamma = 0 \quad (1b)$$

$$\text{at} \qquad t = t_B, \qquad \gamma = \gamma_B \quad (1c)$$

[1] Du Pont Trademark.

This has been done for some special cases which frequently occur in laboratory "tenacity" and "fatigue" measurements. In order to obtain these explicit, though approximate, solutions for Equations 1, it has been assumed that $\Delta F^{\ddagger}$, λ, and δ are independent of t until $t = t_B$. The results are given below.

Case 1. Lifetime under Dead Loads

In this case, the fiber is supporting a fixed load. It very often happens that nearly all of the deformation occurs in a time interval that is negligible compared with t_B, and the stress, f, may be regarded as being a constant. Then the integral of Equations 1 will be

$$t_B = (A/2)\ \text{csch}\ \{Bf\} \tag{2a}$$

$$A \equiv (\gamma_B h/\lambda kT)\ \exp\ \{\Delta F^{\ddagger}/RT\} \tag{2b}$$

$$B \equiv \delta/2kT \tag{2c}$$

If one studies, near room temperature, materials strong enough to be useful in textile technology, then it will, in general, be found that f must be considerably greater than $2kT/\delta$ for fracture to occur in a reasonably short time interval. Equation 2a may then be written

$$\ln t_B = \ln A - Bf \tag{2d}$$

Case 2. Lifetime under Periodic Loads

Here, we consider the general class of experiments in which a fiber is isothermally fatigued under a periodic stress $f(t)$, with period a; that is,

$$f(t \pm na) = f(t) \tag{3}$$

where n is a whole number. It will be assumed that $f(t)$ is never negative (to avoid compression) and that t_B/a is large enough to be represented by an integral number of cycles. We then obtain, from Equations 1 and 3, the following result:

$$t_B = \frac{Aa}{2\int_0^a \sinh\ \{Bf(t)\}\ dt} \tag{4}$$

and, if we put $\theta \equiv t/a$, this becomes

$$t_B = \frac{A}{2\int_0^1 \sinh\ \{Bf(a\theta)\}\ d\theta} \tag{5}$$

Equation 5 may be readily evaluated for some special functional forms of $f(t)$ which are often encountered in laboratory experiments. For example, if

$$f(t) = p + q \sin\left(\frac{2\pi t}{a}\right) \tag{6}$$

with $p > q$, then Equation 5 yields

$$t_B = \frac{A\ \text{csch}\ (Bp)}{2I_0(Bq)} \tag{7a}$$

Here, I_0 is the zeroth order hyperbolic Bessel function. For large Bp, Equation 7a becomes

$$t_B = \frac{Ae^{-Bp}}{I_0(Bq)} \tag{7b}$$

For both Bp and $Bq \gg 1$, we may make use of the asymptotic behavior of I_0 to write

$$t_B = (2\pi Bq)^{\frac{1}{2}} A\ \exp\ \{-B(p+q)\} \tag{7c}$$

Equation 5 may also be evaluated for the case of a fatigue experiment in which $f(t)$ is a "triangular function" of the time with period a and maximum amplitude b:

for $0 \leq t < a$:

$$f(t) = \begin{cases} 2bt/a, & 0 \leq t < a/2 \\ 2b(1 - t/a), & a/2 \leq t < a \end{cases} \tag{8}$$

for $t \geq a$:

$$f(t) = f(t - na)$$

where n is the numer of completed cycles that have elapsed since $t = 0$. In this case, we obtain

$$t_B = \frac{ABb}{2\ \text{cosh}\ (Bb) - 2} \tag{9a}$$

For $Bp \gg 1$, Equation 9a reduces to

$$t_B = ABbe^{-Bb} \tag{9b}$$

An examination of Equations 7 and 9 immediately yields the observation that for the simple fatigue experiments considered here, t_B is independent of a. This observation suggests the following theorem:

Whenever $f(t)$ is periodic and $t_B \gg$ **a**, *t_B is independent of* **a**. The validity of this statement is apparent if we put $\theta \equiv t/a$ into the Fourier series

expansion of $f(t)$,

$$f(t) = \tfrac{1}{2}b_0 + \sum_{n=1}^{\infty} b_n \cos\left(\frac{2\pi nt}{a}\right) + \sum_{n=1}^{\infty} c_n \sin\left(\frac{2\pi nt}{a}\right) \quad (10)$$

and substitute the resulting expression for $f(a\theta)$ into Equation 5:

$$t_B = A\left[2\int_0^1 \sinh\left\{\frac{Bb_0}{2} + B\sum_{n=1}^{\infty} b_n \cos(2\pi n\theta) + B\sum_{n=1}^{\infty} c_n \sin(a\pi n\theta)\right\} d\theta\right]^{-1} \quad (11)$$

Since the right-hand side of Equation 11 is independent of a, the theorem is proven. This theorem represents the most important qualitative prediction of the theory; namely, that if one changes the frequency in isothermal fatigue experiments on oriented polymeric fibers, one will, in general (provided a is kept out of the range of relaxation times of the material being tested), observe that it is the time required for failure, and not the number of cycles to failure, that remains independent of the frequency. Thus, the present theory predicts that textile fibers should have fatigue properties which differ in character from those observed in low temperature measurements on metals where one usually finds that the number of cycles to failure is approximately a constant for given stress limits, regardless of the frequency.

Case 3. Lifetime under Linearly Increasing Loads[2]

Perhaps the most frequently used measures of fiber strength are those obtained from experiments in which samples are subjected to tensile stresses which are monotonic functions of the time. The usual procedure is to let

$$f(0) = 0 \quad (12a)$$

and to build up the load continuously in time until the fiber breaks. The value of the stress at the moment that the fiber breaks is called the tensile strength or "tenacity" of the fiber; we shall use the symbol, f^*, for this quantity:

$$f^* = f(t_B) \quad (12b)$$

Of the various possible functional forms for $f(t)$, the most popular is that of the constant rate of loading experiment, for which

$$f = \alpha t \quad (13a)$$

and

$$f^* = \alpha t_B \quad (13b)$$

where α is the rate of loading.

If we substitute Equation 13a into Equation 1 and use Equation 13b to eliminate t_B, we obtain

$$\cosh(Bf^*) = 1 + B\alpha A/2 \quad (14a)$$

When $Bf^* \gg 1$, Equation 14a reduces to

$$f^* = B^{-1} \ln(B\alpha A) \quad (14b)$$

It is thus seen that for most textile fibers, one should expect the tensile strength to be a linearly increasing function of the logarithm of the rate of loading.

Case 4. Strength Loss in Fatigue Experiments

The following modification of the experiments discussed above is often performed when information is needed about the performance of a fiber under a constant or periodic stress history, $f(t)$, for which t_B is too large to be conveniently measured. In this case, the fatiguing under $f(t)$ is stopped at a time t_F, such that $t_F < t_B$, and the tensile strength of the fiber is measured using, say, the loading history described by Equations 13. The magnitude of the stress at the moment that the fiber breaks under $f = \alpha t$ is the tensile strength of the fatigued fiber. It shall be denoted by f_F^*. In general, f_F^* will be less than the tensile strength, f_0^*, obtained for an unfatigued fiber ($t_F = 0$) at the same value of α. The difference, $f_0^* - f_F^*$, is usually referred to as the strength loss occurring in the time t_F under the loading history $f(t)$.

The question now arises as to what the present theory can predict about the dependence of $f_0^* - f_F^*$

[2] The model used here to derive Equations 14 is similar to one recently proposed by Illingworth and Kilby [5] to discuss the temperature dependence of tensile strength measurements described by Equations 13. The differences between the models are of minor significance. Illingworth and Kilby identify γ_B with one half of the length, L, of the polymer chains and consider a perfectly ordered structure. In the present paper we consider fibers which are neither perfectly oriented nor completely crystalline, and for which γ_B would be expected to be a very complicated function of both the temperature and molecular weight. In reference [2] it is suggested that it might be possible to relate γ_B/λ to the non-recoverable part of the elongation at break. If this is the case, then $\gamma_B/\lambda < 1$, and since the order of magnitude of λ must be the same as the repeat distance between force centers, the equality $\gamma_B = L/2$ would be untenable.

on t_F for a given $f(t)$. It will soon be apparent that we can predict $f_0^* - f_F^*$ for any t_F provided we know the ratio t_F/t_B.

While the fiber is being fatigued under $f(t)$ for the time t_F, the value of γ increases from 0 to γ_F, where γ_F is given by

$$\gamma_F = (2\lambda kT/h)e^{-\Delta F^\ddagger/RT} \int_0^{t_F} \sinh\left\{\frac{f(t)\delta}{2kT}\right\} dt \quad (15)$$

If $f(t)$ is periodic, and if $t_F/a \gg 1$, Equation 15 may be written

$$\gamma_F = (2\lambda kT/h)e^{-\Delta F^\ddagger/RT}(t_F/a) \times \int_0^a \sinh\left\{\frac{f(t)\delta}{2kT}\right\} dt \quad (16a)$$

If $f(t) = f$, a constant, then Equation 15 becomes

$$\gamma_F = (2\lambda kT/h)e^{-\Delta F^\ddagger/RT} \sinh\left\{\frac{f\delta}{2kT}\right\} t_F \quad (16b)$$

If the fiber had been fatigued under $f(t)$ up to the time of fracture, γ would have increased to its upper limit of γ_B, and in place of Equations 16a and 16b, we would have, respectively,

$$\gamma_B = (2\lambda kT/h)e^{-\Delta F^\ddagger/RT}(t_B/a) \times \int_0^a \sinh\left\{\frac{f(t)\delta}{2kT}\right\} dt \quad (17a)$$

$$\gamma_B = (2\lambda kT/h)e^{-\Delta F^\ddagger/RT} \sinh\left\{\frac{f\delta}{2kT}\right\} t_B \quad (17b)$$

Thus, for either constant loads or periodic loads, we have the simple result that

$$\gamma_F/\gamma_B = t_F/t_B \quad (18)$$

At the time t_F, the fiber is removed from the fatigue apparatus and placed in a tensile tester which obeys Equation 13a. It shall be assumed that the temperature and humidity of the tensile strength measurement are not necessarily the same as those for the fatiguing under $f(t)$. Thus, we shall put primes on those quantities which refer to the tenacity determination, and which may be dependent on the thermal and chemical environment. If $t_F = 0$, we have, in place of Equation 14a,

$$\cosh(B'f_0^*) = 1 + B'A'\alpha/2 \quad (19)$$

When $t_F \neq 0$, the calculation of f_F^* requires the integration of Equation 1a using Equation 13a and the following boundary conditions:

when $t = 0$ $\gamma = \gamma_F$ (20a)

when $t = t_B$ $\gamma = \gamma_B$ (20b)

We thus obtain

$$\cosh(B'f_F^*) = 1 + \frac{B'A'}{2}\left\{\frac{\gamma_B - \gamma_F}{\gamma_B}\right\} \quad (21)$$

Equations 19, 21, and 18 yield

$$1 - \frac{t_F}{t_B} = \frac{\cosh(B'f_F^*) - 1}{\cosh(B'f_0^*) - 1} \quad (22a)$$

If $B'f_0^* \gg 1$, and if t_F/t_B differs from unity by a few per cent or more (as is usually the case), then Equation 22a is very well approximated by the following:

$$f_0^* - f_F^* = \frac{1}{B'} \ln(1 - t_F/t_B) \quad (22b)$$

The derivation of Equations 22 involved an assumption which has not previously been introduced into this discussion. It is the assumption that the critical value of γ, γ_B, is independent of temperature and humidity. Experimental work will be required to test the validity of this assumption for particular systems. Of course, if the fatiguing under $f(t)$ and the tenacity measurements under αt are both carried out in identical environments, then this assumption is unnecessary.

The discussion given above accounts for only the effect of uniaxial tensile stresses, $f(t)$. If the adverse environment of a fatigue experiment involves such things as chemical degradation or abrasion due to interfiber friction, then Equations 22 will not apply.

Recapitulation of the Principal Results and Some Limitations

According to the present theory, if one determines the two fundamental parameters A and B (see Equations 2) for a given yarn in a particular environment,[3] then it should be possible, subject to

[3] We may say that the environment of a yarn is known when it has been brought into equilibrium with air of a known relative humidity and temperature, and if its previous stress-strain and thermal history have been characterized. The fact that a yarn may "remember" its past history, as far as mechanical measurements are concerned, is well known. We should not be at all surprised if previous loadings and heatings such as those encountered in drawing and hot-stretching operations, or even the less drastic changes which take place while drawn and/or stretched yarns set on pirns and beams, should affect the measured values of A and B.

certain limitations, to calculate the time required for the breaking of the yarn under any loading history which is carried out in that environment. If the loading history is such that t is a single-valued function of f, as in a tenacity measurement, then the theory can be used to calculate the stress at the moment of fracture. This quantity is called the tensile strength. The theory emphasizes the fact that the tensile strength of a yarn depends on the loading history used in its determination.

It must be emphasized that there are implicit assumptions in Equations 1 which place important limits on the range of validity of the results derived therefrom. When a comparison with experiment is sought, these limits must be taken into account. First of all, when we write Equation 1a, we assume that the mean force acting on a force center is a linear function of the applied stress. This will not be true if any of the following conditions exist: (1) if $f(t)$ varies so rapidly with time that impulsive loading and wave effects need to be considered; (2) if $f(t)$ is periodic with its period, a, approximately equal to the mechanical relaxation times of the test sample; (3) if t_B is of the same order of magnitude as the mechanical relaxation times.

In the case of actual semicrystalline fibers one might expect that Equations 1 represent a very drastic oversimplification of the actual mechanism of mechanical breakdown. It seems, perhaps, more reasonable to postulate the existence, at each cross section, of an array of force centers which can be divided into discrete sets of markedly different character, with the force centers in the ith set possessing the parameters ΔF_i, δ_i and λ_i, and bearing a stress $f_i(t)$ when the applied stress is $f(t)$. If we use such a model, we can still obtain Equation 1a, if we make certain assumptions. This will be clear from the following arguments.[4] The more general model still permits us to write

$$\frac{d\gamma_i}{dt} = 2C_i \sinh \{B_i f(t)\} \tag{23a}$$

where

$$C_i \equiv (\lambda_i kT/h) \exp \{-\Delta F_i^{\ddagger}/RT\} \tag{23b}$$

and

$$B_i \equiv \delta_i/2kT \tag{23c}$$

but little can be done with such expressions, unless we assume something about the relationship between the $f_i(t)$ and $f(t)$. The simplest assumption we can make is that the stresses f_i are linearly related to the applied stress:

$$f(t) = \sum_i \eta_i f_i(t) \tag{24}$$

with coefficients η_i that are independent of t. Then, we can write

$$f(t) = \sum_i (\eta_i/B_i) \sinh^{-1} \left\{ \frac{1}{2C_i} \frac{d\gamma_i}{dt} \right\} \tag{25a}$$

When f is sufficiently large so that all $f_i \gg B_i^{-1}$, Equation 25a reduces to

$$f(t) = \sum_i (\eta_i/B_i) \ln \left\{ \frac{1}{C_i} \frac{d\gamma_i}{dt} \right\} \tag{25b}$$

It is reasonable to assume that all of the force centers in a given cross-sectional region undergo the same rate of displacement until t becomes very close to t_B. Thus, we shall let

$$\frac{d\gamma_i}{dt} = \frac{d\bar{\gamma}}{dt} \tag{26}$$

for all i. Furthermore, if we define the quantities $\bar{B}$ and $\bar{C}$ such that

$$\frac{1}{\bar{B}} \equiv \sum_i \frac{\eta_i}{B_i} \tag{27a}$$

$$\bar{C} \equiv \prod_i C_i^{\eta_i \bar{B}/B_i} \tag{27b}$$

then Equation 25b becomes, after some algebra,

$$\frac{d\bar{\gamma}}{dt} = \bar{C} e^{\bar{B} f(t)} \tag{28}$$

At large values of f, Equations 28 and 1a have the same form.

It will be noticed that the assumption of Equation 24 is absolutely necessary if the slightly more general system described above is to be equivalent to our original model. But once again, Equation 24 can be valid (with the η_i constant) only if both t_B and the period, a, for periodic $f(t)$, are both outside of the range of the relaxation spectrum for motions of the force centers.

Another qualifying restriction must be attached to the relationships derived from Equations 1. It is important to bear in mind that the molecular parameters which enter into the definitions of A and B are not volume average quantities in the

[4] The discussion based on Equations 23 was suggested by the recent work of Ree and Eyring on the theory of viscous flow [8].

usual sense, but rather properties of the weakest cross-sectional region. If values of A and B are calculated for a given yarn by averaging the results of measurements on several samples,[5] one can expect the average values of either A or B, or both, to depend on the size of the test samples [3]. It follows that the use of the theory to predict values of t_B for a particular loading history from values of t_B under a different loading history requires that the yarn samples used in the two tests have the same length and denier.

Perhaps it would also be advisable to suggest some additional precautionary measures, of a purely experimental nature, that must be taken in the testing of phenomenological relationships for mechanical failure such as those predicted here. It is an accepted principle in textile testing technology that the results of a tensile strength test have little significance unless the breaks consistently occur away from the clamps. The same is true, of course, for the measurement of fatigue lives under constant and periodic loads. The experimental difficulties encountered in the elimination of clamp breaks become most severe when periodic loads are used because of the increased possibilities for abrasion at the clamps.

The authors believe that the lifetime-under-dead-load experiment, when used in conjunction with Equation 2d, represents the most convenient method of determining A and B for a given yarn. This is because it permits an extension of the range observation over many decades in t_B, and yet requires only the simplest of experimental apparatus.

The linear relationship between $\ln t_B$ and f predicted by Equation 2d has often been observed in experiments on cotton yarns and filaments [1, 6, 7]. Measurements in this laboratory have confirmed this relationship for high tenacity rayon, drawn Dacron[6] polyester fiber, and drawn nylon. Typical results for Type 300 nylon (consisting of 140 continuous filaments comprising an 840-den. bundle twisted to ½ turns in.$^{-1}$; length of test sample = 25.4 cm.), and Type 200 nylon (15-den. monofil; no twist; length of test samples = 50.0 cm.) are shown in Figure 1. These measurements were

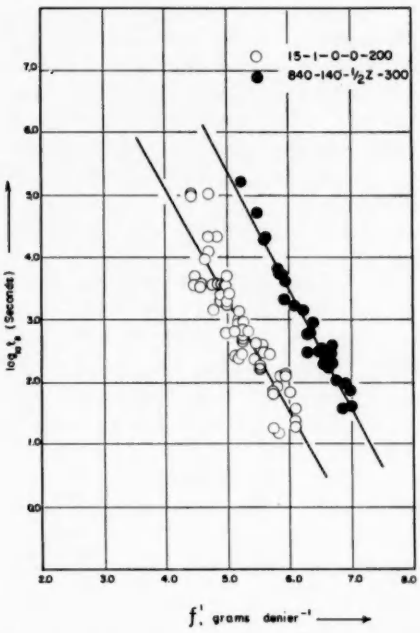

Fig. 1. Plot of the logarithm of the lifetime in seconds versus the dead load in grams denier^{-1} for 66 nylon. Solid circles are Type 300 yarn; open circles are Type 200 yarn. Stresses are calculated using the denier of the unloaded yarn. Each point represents a single break.

made in air at a temperature of 23.3 ± 1° C. and a relative humidity of 72 ± 4%. Least squares analysis of the data gave the following results:

For Type 300 nylon:

$$\log_{10} t_B = 14.90 \pm 0.31 - (1.90 \pm 0.05)f'$$

For Type 200 nylon monofil:

$$\log_{10} t_B = 12.3 \pm 3.1 - (1.8 \pm 0.6)f'$$

The precision limits are probable errors. Here, the stress, f', is in the textile units of grams per denier, based on the denier of the unloaded yarn.

The form of Equations 2d and 14b suggests the general approximate "rule of thumb" that when monotonic loads are used, breaking times should vary exponentially with the stress at rupture regardless of the loading histories used. A general approximate rule of this sort was first proposed by Midgley and Pierce [7] after a careful analysis of the extensive data on cotton collected by Pierce and his co-workers. These data covered a range of seven decades in t_B.

[5] A typical averaging process is the calculation by least squares analysis of the best straight line through a plot of $\ln t_B$ versus f, where the t_B are the experimentally observed breaking times under known f in a series of lifetime-under-dead-load measurements.

[6] Du Pont Trademark.

Recent experiments [2] on drawn nylon have yielded good agreement between measured values of f^* and those calculated from Equation 14b using values of A and B obtained from dead load results and Equation 2d.

The authors recognize that any theory of this sort based on simplified rate process considerations is at best approximate and heuristic. It is hoped, however, that the simplicity of the phenomenological relationships obtained, and their apparent agreement with existing data, will be sufficiently provocative to hasten experimental tests of these relationships on the wide variety of materials being studied in different textile laboratories.

Acknowledgments

The authors are indebted to Drs. Carl E. Black, Bernhard Gross, and William F. McDevit for stimulating discussions. Thanks are due to Mrs. Nancy W. Seitz for the calculations pertaining to the data in Figure 1.

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INDUSTRIAL SECTION

Acid and Alkali Resistance of Partially Acetylated Cotton Fabrics

Edith Honold, Esmond J. Keating, and Evald L. Skau

Southern Regional Research Laboratory,[1] New Orleans, La.

KNOWLEDGE of the acid and alkali resistance is deemed essential in extending the practical use of partially acetylated cotton fabrics. Where the resistance is adequate, such fabrics may prove advantageous for a wide variety of applications which involve exposure to acidic conditions, as, for example, in the manufacture of coated or impregnated materials or when used for pneumatic or liquid filtration. Acetylated cotton has an enhanced resistance to mildew and rot but most of the rot resistance is lost after partial deacetylation [5]. Information on the degree of deacetylation caused by solutions of a wide pH range is important to estimate the serviceability of these fabrics, particularly in uses where rot resistance is paramount.

In order to evaluate the potentialities and limitations of partially acetylated fabrics, systematic data were obtained on the acid resistance of a series of acetylated fabrics by following the changes in selected properties as affected by concentration of the acid, duration of exposure, temperature, and by the acetyl content of the fabric. For alkaline solutions, the data obtained were less complete but nevertheless showed trends indicative of the property changes which might be expected.

Fabrics

A 48 × 44 commercial cotton sheeting, with a conditioned weight of 4.5 oz./sq. yd., was desized and scoured. Six 80- to 100-yd. portions were partially acetylated [2, 3] to obtain six fabrics ranging in acetyl contents from 7.5 to 27.2% acetyl (dry basis) or from 8.1 to 37.4% acetyl (anhydroglucose-residue basis). An unacetylated portion was included for comparative purposes.

Experimental Methods

For establishment of the control values for the seven fabrics, 7-in. strips were cut across each from spaced positions along the length of the bolt and were taken through a routine washing and drying before the determination of the selected properties (Table I). The strips were washed in running tap water for 4 hr., soaked in two successive changes of distilled water (1 hr. each), and air-dried overnight. The test specimens were prepared and slightly dried in order to ensure their equilibration by adsorption when placed under standard conditions (70° ± 2° F. and 65% ± 2% R.H.) for 24 hr. prior to testing.

Steeping Procedures

Sample strips were steeped for different periods of time in selected acid, alkaline, or solvent baths at two different temperatures. For each test, a set of strips, one from each fabric, was steeped together in sufficient solution so that there was approximately 1 liter of solution to each 270 sq. in. of fabric. After removal from the bath, the group as a whole was taken through the routine washing and drying to minimize continued action of the steeping solution during subsequent conditioning prior to testing. The

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

TABLE I. Control Values for Selected Properties of the Seven Untreated Fabrics

Fabric No.	Acetyl*, %	Moisture*, %	Breaking strength†, lb.	Tearing strength, lb.	Elongation at Break†, in.	Modulus‡
0	0.0	6.5	58.2 ± 2.3	6.4 ± 0.3	0.458 ± 0.022	0.53×10^{-2}
1	8.1	5.7	65.6 ± 2.4	3.1 ± 0.1	0.333 ± 0.012	0.37
2	9.1	5.2	57.5 ± 2.9	2.9 ± 0.2	0.341 ± 0.017	0.41
3	16.8	4.4	53.5 ± 2.4	2.4 ± 0.1	0.314 ± 0.011	0.42
4	19.8	4.2	50.4 ± 2.6	2.3 ± 0.1	0.343 ± 0.012	0.46
5	28.6	4.1	56.0 ± 2.6	2.5 ± 0.1	0.410 ± 0.016	0.46
6	37.4	3.8	50.2 ± 2.6	2.0 ± 0.1	0.498 ± 0.017	0.56

* Expressed as grams per 100 g. of anhydroglucose residue.
† Determined on strips raveled to 48 warp threads.
‡ Inch increase per pound in 3-in. lengths on linear portion of tensilgram.

samples which were steeped in the two chlorinated hydrocarbons were shaken in three changes of 95% ethanol after removal from the steeping baths and before washing.

Test Methods

The breaking strengths and elongations at break were measured on a pendulum-type tester, using specimens which had been raveled to 48 warp threads. The Elmendorf method [1] was used to measure warp tearing strengths. The control values for the three properties are the averages of 20, 20, and 6 tests, respectively.

Per cent acetyl was determined by the Eberstadt method as modified by Genung and Mallatt [4]. Per cent moisture regain was calculated from the loss in weight after drying in a forced-draft oven for 5 hr. at 105° C. Both sets of data were converted to the anhydroglucose-residue basis whereby the acetyl content or the moisture sorbed is shown as grams of acetyl or water per 100 g. of anhydroglucose residue.

Results and Discussion

Control Values

In most instances, the variation in property values from position to position along the bolt lengths was insignificant but in a few, slight trends were evident. Table I lists the values at one bolt position for each fabric.

The breaking strength fluctuated somewhat but exhibited an over-all tendency to decrease as the acetyl content was increased. This cannot be accepted as a generality, because in a similar group of fabrics [6], the breaking strength had been found to increase as the acetyl content was increased. The change in breaking strength with increased acetylation evidently is affected by fabric weight and construction and by inadvertent differences in processing.

The tearing strength, in the present series, was reduced 50% by the addition of 8.1% acetyl and was further reduced as the acetyl content was increased.

A plot of the elongation-at-break values against per cent acetyl resulted in a curve which passed through a minimum at about 12–13% acetyl. Since the ultimate elongation is somewhat dependent upon the load at which the specimen breaks, the slope of the straight-line portion of each tensilgram was estimated as elongation per pound. This modulus for the fabric of lowest acetyl content (No. 1, 8.1% acetyl) was considerably less than that of the unacetylated fabric. There was an upward trend as the degree of acetylation was increased, until the modulus of the fabric of highest acetyl content (No. 6, 37.4% acetyl) was greater than that of the unacetylated fabric.

Hydrochloric Acid Solutions

The effects of hydrochloric acid at room temperature (27° ± 4° C.) were studied in the greatest detail. Complete sets of specimens were steeped in 0.5 *N*, *N*, or 2 *N* solutions for 1, 3, 5, 7, or 10 days, and all the selected properties were determined.

Deacetylation

The deacetylation of the fabrics was dependent upon the strength of the acid, the original acetyl content, and the duration of steeping. These parameters are combined in Figure 1 by plotting the loss in acetyl percentage after each treatment against the

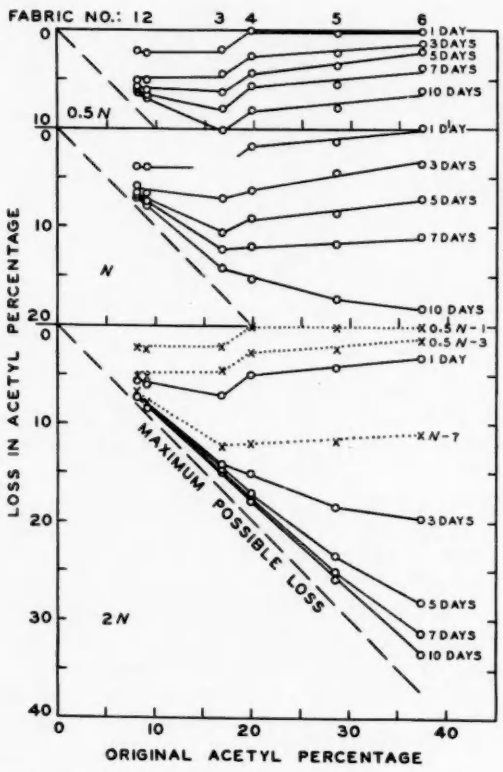

Fig. 1. Loss of acetyl after treatment with 0.5 *N*, *N*, and 2 *N* hydrochloric acid solutions at room temperature. All acetyl contents are expressed as grams of acetyl per 100 g. of anhydroglucose residue.

original acetyl percentage. Most noteworthy is the break between the 16.8%-acetyl and the 19.8%-acetyl fabrics (Nos. 3 and 4). The more highly acetylated Fabric 4 lost less acetyl than Fabric 3 after those treatments in which the acetyl percentage was reduced by less than 12. Each triad of fabrics on either side of the break followed a different deacetylation pattern. Those of lower acetyl content lost approximately equal amounts of acetyl when the acetyl percentage was decreased by less than 6 and, thereafter, lost acetyl in proportion to the original acetyl content. The fabrics of more than 19% acetyl lost quantities which were inversely related to the original acetyl content until the acetyl percentage had been lowered by approximately 12. When the acid treatment was more severe, all six fabrics were included in the generalization that the loss of acetyl was greater the higher had been the original acetyl content of the fabric and, eventually, in the strongest acid for the longest period of time (2 *N*, 10 days), the losses from all fabrics were proportional to the original acetyl contents. Under the conditions of these experiments, none of the partially acetylated fabrics was ever deacetylated completely in the acid solutions, and the unacetylated fabric actually picked up 1% acetyl after 5, 7, or 10 days in 2 *N* hydrochloric acid.

The severity of any treatment may be considered to be synonymous to the "deacetylating capacity" which is seen (Figure 1) to be a function of both acid concentration and of steeping time. The 2 *N*, 1-day; *N*, 3-day; and 0.5 *N*, 7-day treatments had almost the same deacetylating capacities and illustrate a balancing between the two variables, so that a decreased acid concentration compensated for the increased steeping time.

Strength Changes

The breaking strength and the tearing strength of each fabric were reduced after treatment and the per cent retention in each case was related to the degree of deacetylation, as shown in Figures 2, A and B. However, no general relationship including the data from all the acetylated fabrics is apparent between the degree of deacetylation and per cent–strength retention since a given loss in acetyl percentage was accompanied by a higher per cent–strength retention when the original acetyl content of the fabric had been high.

In general, the higher the original acetyl content of the fabric, the smaller was the strength-reducing effect of any individual acid treatment, or the greater was the severity of treatment (with respect to either time of steeping and/or concentration of acid) which produced a given per cent reduction in strength (Figure 3). The 8.1% acetyl of Fabric 1 apparently offers no protection to breaking strength since the curves for this fabric coincide with those of the unacetylated fabric; however, this degree of acetylation does show considerable protection of tearing strength. From these groups of curves, the conclusion can be drawn that the more highly acetylated a fabric, the more slowly does it loose strength in a given acid solution.

Both strength-retention percentages of those fabrics acetylated to more than 9% (Nos. 2 to 6) always exceeded those of the corresponding unacetylated fabric specimens. For a given fabric, this improve-

ment in strength retention increased progressively to a maximum and then decreased as the acid treatment became more severe, the improvement at the maximum being the greatest for the most highly acetylated fabric. By assuming, as implied above, that the degree of deacetylation of a given fabric is a measure of the severity of the acid treatment, the relationships established in the previous figures can all be combined into a generalized representation by plotting the breaking-strength and the tearing-strength data in the manner used in Figures 4 and 5, respectively. In each graph, the per cent acetyl remaining in a specimen after each treatment is plotted against the per cent–strength–retention difference, i.e., the strength-retention percentage of each acetylated fabric minus that of the unacetylated fabric which had been subjected to the same treatment.

The point of maximum difference for each fabric is approached along an individual curve, and for more severe treatments, all specimens of all fabrics tend to

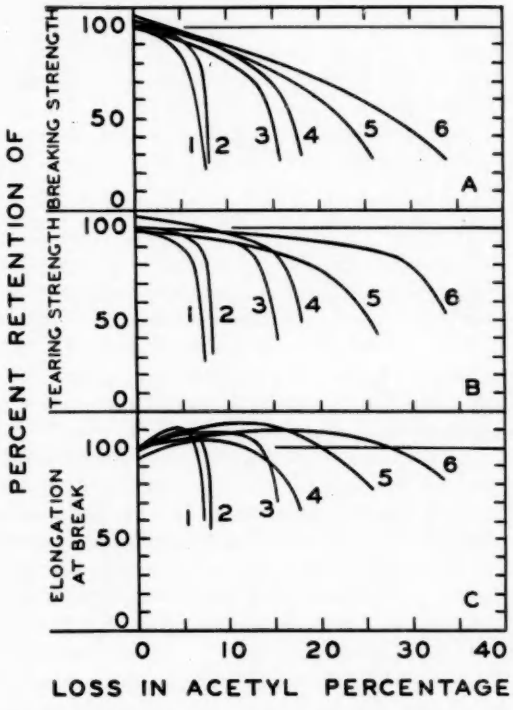

Fig. 2. The effect of hydrochloric acid treatment on the physical properties of the fabrics, relating the per cent retentions to the loss in acetyl percentage. The numbers identify the fabrics.

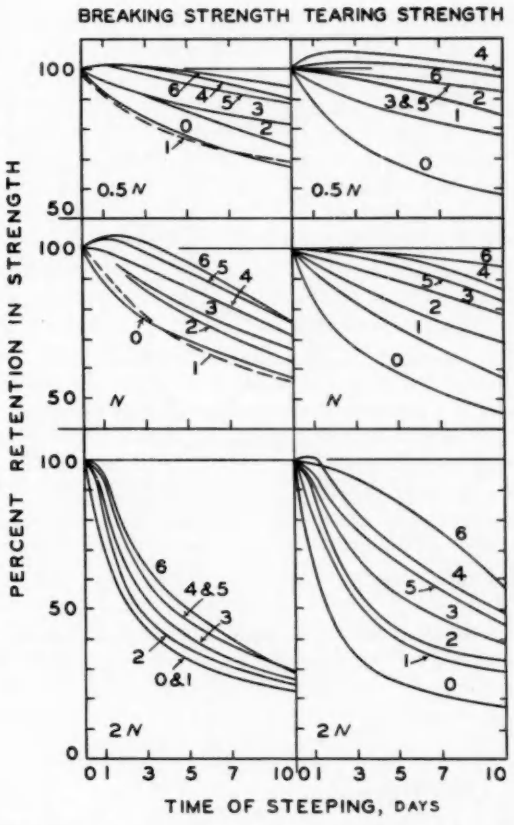

Fig. 3. Per cent retention in breaking strength and in tearing strength as the time of steeping is prolonged in the various hydrochloric acid solutions at room temperature. The numbers identify the fabrics.

fall on the common lower curve which shows a decrease in per cent–strength–retention difference as additional acetyl groups were removed and which approaches 1% acetyl asymptotically. While Figures 4 and 5 resemble each other in a very general way, they show considerable differences. The maximum per cent–strength–retention differences of the tearing-strength curves are more than twice those of the breaking-strength curves and were reached after greater deacetylation. A maximum difference in the breaking-strength relationships for each fabric occurred after a reduction of 6 to 8 in acetyl percentage, while approximately $\frac{3}{4}$ of the original acetyl content of each fabric was removed at the maximum in its tearing-strength curve. Thus, in contrast to a fixed loss of acetyl (about 6 to 8 g. per 100 g. of anhydro-

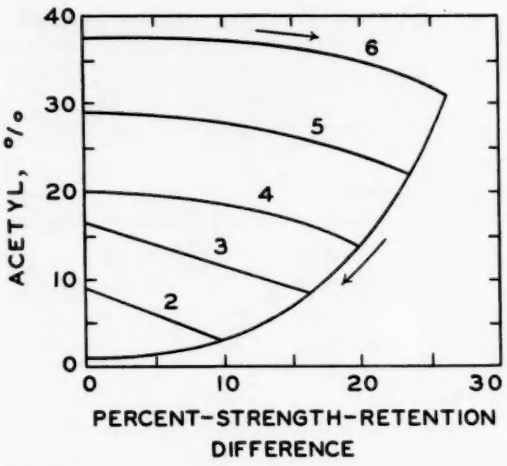

Fig. 4. A representation of breaking-strength protection as related to degree of acetylation, *i.e.*, the per cent acetyl retained versus the additional strength-retention percentage of each fabric over that of the unacetylated fabric after the hydrochloric acid treatments at room temperature. The numbers identify the fabrics.

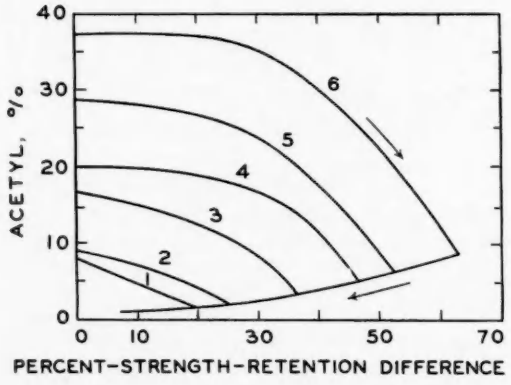

Fig. 5. A representation of tearing-strength protection as related to degree of acetylation, *i.e.*, the per cent acetyl retained versus the additional strength-retention percentage of each sample over that of the unacetylated sample after the hydrochloric acid treatments at room temperature. The numbers identify the fabrics.

glucose residue) at the maximum differences in the breaking-strength curves, the losses of acetyl at the corresponding points in the tearing-strength curves varied with the fabric.

For the unacetylated fabric, the per cent losses in tearing strength after treatment were greater than those in breaking strength. The reverse is evident for the acetylated fabrics; in addition, the per cent

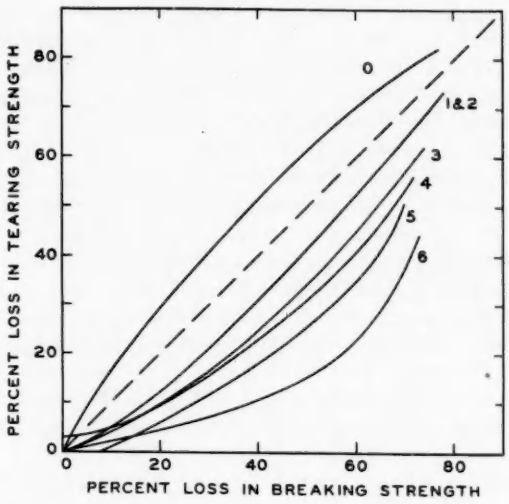

Fig. 6. Relationship between the per cent losses in breaking strength and in tearing strength after treatments with hydrochloric acid at room temperature. The broken line represents theoretically equal losses in both strengths. The numbers identify the fabrics.

losses of tearing strengths tended to be increasingly less than those of breaking strengths in the same order as increasing acetyl content of the untreated fabrics (Figure 6).

Elongation at Break

As the severity of the acid treatment was increased, the elongation at break of each acetylated fabric increased to a maximum and then decreased to values below that of the untreated fabric (Figure 2, C). In general, the higher the original acetyl content, the greater was the loss of acetyl before the reduction in elongation was observed.

The elongation at break for the unacetylated fabric decreased after steeping in the acid solutions (Figure 7), and a linear correlation was noted between these values and the breaking-strength data so that a 0.75% loss in elongation accompanied a 1% loss in breaking strength. The elongation at break of Fabric 6 (37.4% original acetyl) not only surpassed the value of the unacetylated fabric when both were in the untreated state but always maintained a higher value than the unacetylated after acid treatment. With the exception of the mildest acid treatment, Fabric 5 (28.6% original acetyl) likewise reached and maintained elongation-at-break values which were greater than

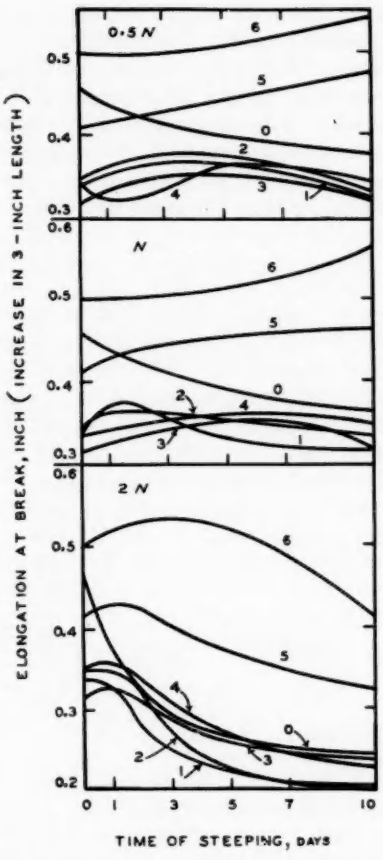

Fig. 7. Elongations at break as the time of steeping is prolonged in the various hydrochloric acid solutions at room temperature. The numbers identify the fabrics.

those for the corresponding unacetylated specimens. The remainder of the partially acetylated samples showed elongations at break which were lower than, or approximately equal to, those of the corresponding unacetylated specimens. However, on a percentage-wise basis, all the acetylated fabrics retained more of their original elongations at break after acid treatment than the unacetylated fabric.

Moisture Sorption

Moisture sorption percentages were determined after exposure at standard conditions. Since the moisture sorbed has been calculated on the basis of the anhydroglucose residue, the percentages obtained for the partially acetylated fabrics are higher than moisture regain values which are calculated on the basis of dry sample weight.

As shown in Table I, the higher the acetyl percentage of the untreated fabrics, the lower was its moisture sorption. The rate at which the sorptive capacity decreased with respect to acetyl content changed abruptly in the vicinity of 18% acetyl, so that the initial rate was approximately six times that of the final rate (Figure 8). The initial slope of the broken line corresponds to a decrease of 0.3 molecule of water for each acetyl group added, while the final slope is equivalent to a decrease of only 0.05 molecule of water per acetyl group.

None of the hydrochloric acid treatments caused any appreciable change in the moisture sorption of the unacetylated fabric, all the values being within acceptable experimental limits ($\pm 0.25\%$) of the average value of 6.5%, as shown by the dotted lines in Figure 8. In contrast, the moisture sorbing capacity of each partially acetylated fabric was increased after acid steeping. As a fabric was deacetylated progressively, the moisture percentage rose to a maximum value which was greater than that of the unacetylated and then decreased by a fraction of a percentage. Each successive fabric, i.e., in the order of increasing *original* acetylation, reached a higher maximum sorption after partial deacetylation than the previous

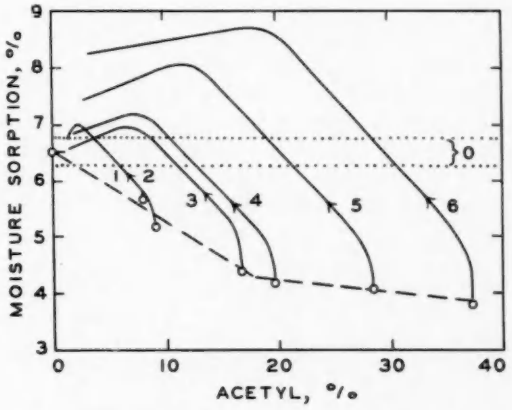

Fig. 8. The moisture sorptions of the fabrics before and after hydrochloric acid treatments as related to the acetyl percentage. The moisture or the acetyl is expressed as grams of water or acetyl per 100 g. of anhydroglucose residue. The broken line connects the untreated fabrics, and each solid line shows the change in moisture sorption for each individual fabric as the acetyl percentage is decreased. The dotted lines encompass all values for the unacetylated fabric after all treatments. The numbers identify the fabrics.

fabric, until Fabric 6 (37.4%, original acetyl) reached a maximum sorption of almost 9% moisture or about 2.5% more than that of the unacetylated fabric.

The data for Fabrics 1 and 2 were insufficient to delineate the initial rising curve, since the mildest acid treatment brought both moisture percentages within the range of the unacetylated fabric. The values for Fabric 1 remained within the limits set for the unacetylated fabric except for only one value of 7.1% moisture at 2.5% acetyl content. The moisture sorptions of Fabrics 2 and 3 decreased from their maxima into the unacetylated range at low acetyl percentages. An immediate gain in sorption was observed in the three fabrics of highest original acetyl content (Nos. 4, 5, and 6) even before there was any perceptible or significant reduction in acetyl. When significant quantities of acetyl had been removed, the moisture sorptions for these three fabrics increased at approximately the same rate with respect to acetyl loss so that 0.5 molecule of water was sorbed for each acetyl group removed. These generalizations might justifiably be extended to include Fabric 3. One other generalization, which includes all six fabrics, is that the loss of acetyl at the point of maximum water sorption was progressively greater the higher the original acetyl content of the fabric had been.

The sorptive capacity of a fabric of given acetyl percentage was dependent upon whether the acetyl content had been reached by direct acetylation or by deacetylation from a higher acetyl content and, in the latter instance, was further dependent upon the acetyl percentage from which it had been deacetylated. For example, on the basis of Figure 8, a fabric of 20% acetyl value could have a moisture sorption ranging from 4.25% to higher than 8.5% depending upon its previous history. Acetylation apparently altered the structure of the cotton so that, upon subsequent removal of some of the acetyl groups by acid, the partially deacetylated cotton could sorb more water than the unacetylated cotton. Under the conditions of these experiments, those fabrics of original acetyl value of more than 18% never returned to the range of the unacetylated fabric. Therefore, the conclusion is indicated that their structure had been permanently altered to permit the sorption of additional moisture.

Other Acids at Room Temperature

Results were obtained for similar 1-day experiments using 4 *N* or 2 *N* sulfuric acid or 2 *N* or *N* nitric acid. The data for the 2 *N* nitric acid were limited to acetyl values. The majority of the data was in agreement with Figures 2, 6, and 8, but many of the values lay within the regions of the curves where minor differences were indistinguishable. However, some differences in trend can be shown by comparison with the data obtained from the 1-day experiments in 2 *N* or *N* hydrochloric acid.

Deacetylation

Neither 4 *N* nor 2 *N* sulfuric acid caused as much deacetylation as 2 *N* hydrochloric acid (compare Figures 1 and 9). In fact, there was no appreciable change in acetyl for the three most highly acetylated fabrics (Nos. 4, 5, and 6). The 2 *N* and *N* nitric acid treatments, on the other hand, caused considerably more deacetylation, respectively, than the 2 *N* and *N* hydrochloric acid treatments, the difference being increasingly greater in the order of original acetyl contents of the fabrics. For example, the losses of acetyl from Fabrics 4, 5, and 6 after 2 *N* hydrochloric acid were 5.0, 4.3, and 3.3%, respectively, as compared with 11.2, 13.6, and 15.6% after 2 *N* nitric acid.

Strength Changes

For each fabric, a given loss in acetyl resulting from a 1-day steeping in 4 *N* or 2 *N* sulfuric acid or in *N* nitric acid was accompanied by approximately the same percentage reduction in breaking strength or in tearing strength as that hydrochloric acid treatment which caused the same loss of acetyl. For these comparatively mild acid treatments, the order of the three acids for reducing strength paralleled qualita-

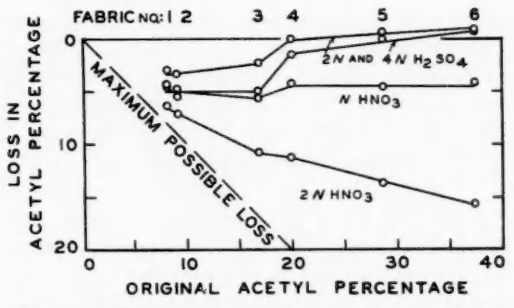

Fig. 9. Loss of acetyl after 1-day steeping in sulfuric or nitric acid solutions. All acetyl percentages are expressed as grams per 100 g. of anhydroglucose residue.

tively the order of their deacetylating capacities. Figure 10 shows that all seven fabrics retained more breaking strength, in this limited range, after either sulfuric acid treatment than after the 2 *N* hydrochloric acid steeping and retained less breaking strength after the *N* nitric acid treatment than after the *N* hydrochloric acid treatment. The tearing-strength comparisons were similar except that the per cent retentions for the two *N* acids, i.e., nitric and hydrochloric, were approximately the same.

Again the acetylated fabrics retained greater percentages of their strengths than the unacetylated fabric. In terms of Figures 4 and 5, most of the sulfuric acid data agreed with the hydrochloric acid curves except those for the three most highly acetylated fabrics after the 4 *N* sulfuric acid treatment. The high acetyl content of this triad protected their breaking and tearing strengths against this sulfuric acid treatment to a greater extent than against any other acid treatment. In contrast, acetylation afforded least protection against the nitric acid treatment in all fabrics.

Elongation at Break

In general, the elongations at break for the unacetylated fabric decreased after these acid treatments, while most of those for the acetylated fabrics increased. The changes frequently were of little significance, but a comparison of the *N* solutions showed a tendency for the elongations to increase somewhat more after the nitric acid treatment than after the hydrochloric acid treatment.

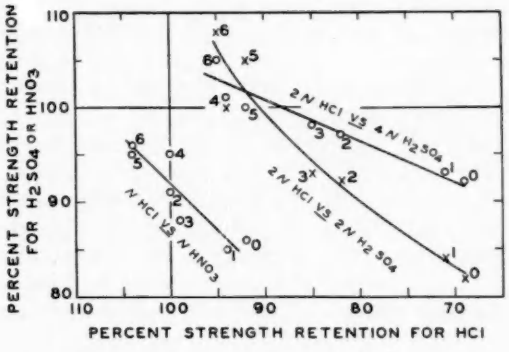

Fig. 10. Per cent retentions of breaking strength after hydrochloric acid treatments compared with the retentions after sulfuric acid or nitric acid treatment. In each acid, the fabrics were steeped for 1 day at room temperature.

Moisture Sorption

The moisture sorption values after both sulfuric acid treatments were in agreement with the hydrochloric acid results as depicted in Figure 8. After the *N* nitric acid treatment, the moisture sorption percentages of all seven samples are placed at slightly higher positions for the quantities of acetyl lost.

Extending the pH Range into the Alkaline Region

The experiments were extended into the alkaline range, using only the unacetylated, the 16.8%-acetyl, and the 28.6%-acetyl fabrics (Nos. 0, 3, and 5). Specimens were steeped for 10 days in 0.1 *N* citric acid (pH = 2.4), for 1 day in 0.1 *N* sodium bicarbonate (pH = 8.7), 0.1 *N* borax (pH = 9.2) or 0.1 *N* sodium carbonate (pH = 11.0), for 1 or 6 days in ammonium hydroxide (pH = 11.7) or for 1 or 2 days in 0.5 *N* sodium hydroxide (pH > 13.0).

The break in deacetylation pattern as shown in Figures 1 and 9 seems to be repeated here in that the 16.8%-acetyl fabric (No. 3) consistently lost more acetyl than the 28.6%-acetyl fabric (No. 5) when the acetyl percentage had been reduced by less than 12 (Table II). For the pH range from 2.4 to 9.2, the acetyl percentages were changed within ± 1% for both samples. Beyond this range in either direction, the losses were increased.

The alkaline treatments tended to maintain or to increase the strength and elongation values of the unacetylated fabric in contrast to the lowering of these values by the acid treatments. The ammonium hydroxide was the only alkaline solution which produced an appreciable loss in tearing strength or in elongation at break for the unacetylated fabric.

In general, the partially acetylated fabrics retained more breaking strength than the unacetylated after acid treatments, and less after alkaline treatments. However, the strength retentions in the alkaline solutions were considerably higher than those in the acid solutions when comparable quantities of acetyl had been removed. For example, the sodium carbonate solution and the 0.5 *N*, 5-day hydrochloric acid treatment removed approximately the same quantity of acetyl from Fabric 3, but the breaking-strength retention after the alkaline solution was higher than after the acid treatment. A similar comparison can be made for Fabric 5 between the ammonium hydroxide, 6 days, and the 2 *N*, 5-day hydrochloric acid treatments. The 0.5 *N* sodium hydroxide treat-

TABLE II. Experimental Data of Selected Properties after Steeping in Alkaline Solutions at Room Temperature. A Few Data for Some Acid Treatments are Included for Comparison

		Acetyl*, %			Moisture*, %			Breaking strength†, lb.			Tearing strength, lb.			Elongation at break†, in. (3-in. length)		
Fabric number		0	3	5	0	3	5	0	3	5	0	3	5	0	3	5
Control values		0.0	16.8	28.6	6.5	4.4	4.1	58.2	53.5	56.0	6.4	2.4	2.5	0.458	0.314	0.410
Solution	Days							Retention, %								
0.1 *N* sodium bicarbonate	1	0.0	16.2	29.2	6.5	4.6	4.0	98	100	98	102	100	99	94	93	86
0.1 *N* borax	1	0.0	16.7	28.7	6.5	5.0	4.4	99	101	102	97	99	96	106	96	98
0.1 *N* sodium carbonate	1	0.0	10.9	27.9	6.7	6.2	4.7	102	95	98	96	96	99	102	109	99
N ammonium hydroxide	1	0.0	9.6	26.0	6.7	6.2	5.4	104	95	101	85	97	98	84	89	85
N ammonium hydroxide	6	0.0	1.7	5.0	6.6	6.8	7.2	103	96	87	88	106	98	85	97	95
0.5 *N* sodium hydroxide	1	0.0	0.0	0.0	6.7	6.7	7.1	94	84	77	107	108	113	99	123	107
0.5 *N* sodium hydroxide	2	0.0	0.0	0.0	6.7	6.7	7.1	101	84	78	112	111	109	103	118	103
0.5 *N* sodium hydroxide	2‡	0.0	0.0	0.0	6.7	6.7	7.2	95	86	78	96	111	110	100	114	102
0.5 *N* hydrocholoric acid	1	0.0	14.8	28.3	6.7	5.4	4.6	95	98	103	91	97	96	90	107	98
0.5 *N* hydrochloric acid	3	0.0	12.3	26.2	6.4	6.1	5.3	81	89	99	73	97	96	87	107	106
0.5 *N* hydrochloric acid	5	0.0	10.5	25.0	6.7	6.5	5.9	78	90	93	71	96	97	90	111	110
2 *N* hydrochloric acid	5	0.8	2.3	5.1	6.7	6.8	7.7	36	40	44	26	54	65	58	84	87

* Expressed as grams per 100 g. of anhydroglucose residue.
† Determined on strips raveled to 48 warp threads.
‡ Fresh solution each day.

ments caused complete deacetylation and reduced the breaking strengths of Fabrics 3 and 5 by 15 and 22%, respectively; in contrast, neither fabric was deacetylated completely in any acid treatment, but comparable reductions in breaking strength were noted after losses in acetyl percentages of only 8 and 14, respectively (Figure 2, A). Thus, the loss in breaking strength is not wholly dependent upon the deacetylating capacities of the treatments.

The tearing-strength-retention percentages for the acetylated fabrics, in most instances, exceeded those of the corresponding unacetylated specimens after either acid or alkaline treatments.

The elongation-at-break values of Fabrics 3 and 5 after complete deacetylation in 0.5 *N* sodium hydroxide were unique in that they had increased considerably over their untreated values. In the acid treatments, as the specimens approached low acetyl contents their elongations at break decreased.

Elevated Temperature, 50° C.

Sets of specimens from the partially acetylated fabrics were steeped at 50° C. for 1 or 3 days in 0.5 *N* hydrochloric acid or for 1 day in 2 *N* sulfuric acid, 0.1 *N* sodium bicarbonate, or 0.1 *N* sodium carbonate and the reduction in acetyl was determined.

Deacetylation

As expected, larger quantities of acetyl were removed from the fabrics at 50° C. than had been removed by the corresponding treatments at room temperature. From the losses as plotted in Figure 11, the break again is evident between the 19.8%-acetyl fabric (No. 4), and the 16.8%-acetyl fabric (No. 3), in that the former lost less acetyl than the latter.

The mildest treatment (sodium bicarbonate) removed approximately equal quantities of acetyl from Fabrics 1, 2, and 3, and negligible amounts from Fabrics 4, 5, and 6. These losses were virtually the same after 0.5 *N*, 1-day hydrochloric acid treatment at room temperature, and the values for the two treatments almost coincide.

The acetyl losses after the two hydrochloric acid treatments at 50° C. approximate those at room temperature after stronger acid solutions and/or longer periods of steeping. The results for 0.5 *N* hydrochloric acid at 50° C. for 1 day and for 3 days (Figure 11) are comparable to those for room temperature treatments (Figure 1) with 2 *N* hydrochloric acid for 1 day and *N* acid for 7 days, respectively.

At 50° C., the progressively greater resistance to deacetylation exhibited by the three most highly acetylated fabrics was slightly heightened in the case

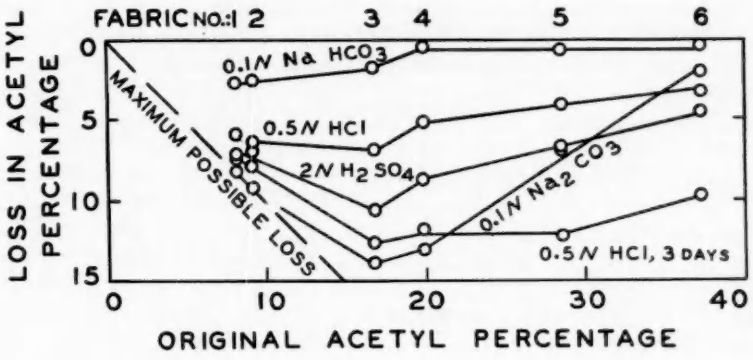

Fig. 11. Loss of acetyl after steeping in various solutions at 50° C. All treatments except one were 1-day steeps.

of sulfuric acid and markedly increased in the case of sodium carbonate.

Other Property Changes

One complete set of specimens (including the unacetylated) was steeped for 1 day in 0.5 *N* hydrochloric acid at 50° C. and all the selected properties determined.

In general, the effect was found to be considerably greater than after the corresponding treatment at room temperature, being comparable rather to hydrochloric acid treatments of greater severity (Table III). The columns under room temperature in Table III are arranged in the order of increasing severity, the 2 *N*, 3-day treatment being the next in order after the *N*, 10-day treatment.

As was pointed out previously, the loss in acetyl percentage for each fabric closely approximated the 2 *N*, 1-day room temperature treatment, but the effect on breaking strength, tearing strength, or elongation at break was more pronounced and the majority of the retention percentages fell within the general range of the more severe *N*, 10-day treatment. The elongation-at-break retentions for Fabrics 5 and 6 approximated room temperature treatments of greater severity, being comparable to the results obtained after 2 *N*, 3 days and 2 *N*, 7 days, respectively. On the other hand, the breaking strengths which deviated from the *N*, 10-day range again showed the advantage of a higher original acetyl content since the retention percentages at 50° C. were comparable to those of room temperature treatments of less severity than the *N*, 10-day treatment. (Compare with *N*, 7 days for Fabrics 3, 4, 5 and with *N*, 5 days for Fabric 6.)

From the breaking-strength data in Table III, the per cent–strength-retention difference at 50° C. between Fabric 6 (37.4% original acetyl) and the unacetylated fabric is 43% or twice the value of 21%, as read from Figure 4 for a hypothetical treatment of the same deacetylating capacity at room temperature. The corresponding values from the tearing-strength data are 52% at 50° C. and 32% at room temperature, the latter as read from Figure 5. Similar improvements in both strength values, but to a successively smaller degree, can be shown for Fabrics 5 and 4, so that the general conclusion can be reached that the higher acetyl contents impart to a cotton fabric a resistance to hydrochloric acid which is greater at 50° C. than at room temperature.

The changes in per cent moisture are approximately the same as those for room temperature treatments which resulted in the same loss of acetyl. The values can therefore be predicted, with fair accuracy, from the acetyl percentages by referring to Figure 8.

Solvents

A few experiments were performed in which organic solvents were used as the steeping baths. Acetyl percentages of all the partially acetylated fabrics were determined after 1 day in acetone at room temperature. Fabrics 3 and 5 (16.8 and 28.6% acetyl) were treated with tetrachloroethylene for 1 day both at room temperature and at 50° C., and the acetyl percentages, the breaking strengths, and the elongations at break determined. In none of these tests was any significant change observed. Fabrics 3 and 5 were also treated with symmetrical tetrachloroethane for 1 day at 50° C. The subsequent tests showed that the acetyl changes were negligible, and

TABLE III. Comparison of Effects on Property Values after Treatment at 50° C. with Results after Treatments at Room Temperature

Fabric number	Control values	Retention percentages after hydrochloric acid treatments at 50° C. 0.5 *N* 1 day	Room temperature (27° ± 4° C.) 0.5 *N* 1 day	*N* 5 days	*N* 7 days	*N* 10 days	2 *N* 3 days	2 *N* 7 days
Breaking strength of 48 warp threads								
0	58.2*	51	95	70	65	*57*		
1	65.6	53	92	68	63	*55*		
2	57.5	64	100	78	70	*63*		
3	53.5	77	98	82	*75*	67		
4	50.4	82	107	87	*80*	72		
5	56.0	89	103	93	*86*	75		
6	50.2	94	103	*95*	85	79		
Tearing strength, warp								
0	6.4*	43	91	61	53	*44*		
1	3.1	57	96	77	70	*56*		
2	2.9	67	100	80	80	*68*		
3	2.4	81	97	89	87	*78*		
4	2.3	87	108	99	93	*88*		
5	2.5	91	96	96	*92*	83		
6	2.0	95	104	99	*96*	*96*		
Elongation at break of 48 warp threads								
0	0.458†	75	90			*83*	*63*	57
1	0.333	89	105			*94*	*73*	62
2	0.341	88	106			*100*	*81*	62
3	0.314	98	107			*102*	*87*	82
4	0.343	95	93			*104*	*88*	71
5	0.410	94	98			113	*97*	88
6	0.498	97	99			112	107	*98*

* Control values in pounds.

† Control values in inch elongation per 3-in. length.

Note: The italicized percentages under room temperature treatments are those results which correspond most closely to the results observed at the elevated temperature.

that the changes in breaking-strength and elongation-at-break values for Fabric 3 were insignificant. However, the breaking strength of Fabric 5 was reduced 22% and the elongation at break was increased 50%.

Summary

The acetyl content of the partially acetylated fabrics determined, to a considerable extent, the changes in property values after exposure to acid or alkaline solutions. The acid resistance of the high-acetyl fabrics was markedly greater than that of the low-acetyl fabrics. The property changes were related, in a general way, to the degree of deacetylation caused by the steeping solutions. Under the experimental conditions investigated, the deacetylation was negligible in solutions having a pH within the range of 2.4 to 9.2, and became more pronounced as the steeping solutions were increased in acidity or alkalinity beyond this range. The fabrics of high acetyl content tended to be more resistant to deacetylation. However, the relationship between original acetyl content and resistance was not regular since a decided break occurred at approximately 18% acetyl (anhydroglucose-residue basis). Throughout the experiments, differences were noted between the behavior of the three fabrics of lower acetyl content (8.1, 9.1, and 16.8%), and those of higher acetyl (19.8, 28.6, and 37.4%).

This break at about 18% acetyl was already apparent in the moisture behavior of the original series of acetylated fabrics. The moisture sorptive capacity of the cotton was reduced in the ratio of 0.3 molecule of water for each acetyl group added until about 18% acetyl had been reached. Thereafter, the sorptive

capacity was reduced at a lower rate so that the ratio approximated 0.05 molecule of water for each additional acetyl. The sorptive capacity increased with comparative rapidity as the fabrics were deacetylated, reaching a maximum moisture sorption value which was successively higher for each fabric in the order of increasing original acetyl percentage. As complete deacetylation was approached, the moisture sorptive capacity of the three most highly acetylated fabrics still remained above that of the unacetylated fabric. The conclusion is justifiable that the structure of the cotton is permanently altered by the introduction of more than 18% acetyl so that additional moisture can be sorbed after the removal of the acetyl groups.

From the systematic data obtained for the hydrochloric acid solutions, patterns were discernible for property changes in relation to severity of acid treatment. The deacetylation pattern, for example, was separated into low-acetyl and high-acetyl groups. The latter was more resistant to deacetylation in the milder acid treatments. The low-acetyl group lost acetyl in approximately equal amounts after any given treatment until 6% acetyl had been removed and thereafter lost acetyl in proportion to the original acetyl percentage. The high-acetyl group lost quantities which were inversely related to the original acetyl until 12% had been removed and thereafter the relationship was reversed so that the acetyl loss became greater the higher the original content. The less detailed data with other reagents and/or higher temperature followed this same general pattern.

The breaking-strength and tearing-strength protection against hydrochloric acid solutions increased with the degree of original acetylation. The data for the other acid treatments followed this general pattern to a greater or less degree depending upon the acid. The data from the sulfuric acid experiments, for example, again differentiated between the low-acetyl and the high-acetyl groups in that the latter showed greater protection against sulfuric acid than against hydrochloric acid, while the results from the low-acetyl group were approximately the same for both acids. A similar observation was made in the comparison of the results at 50° C. with those at room temperature. The major departure from the generalized patterns occurred in the breaking-strength data after alkaline treatments because the breaking-strength retentions of the partially acetylated fabrics were less than the corresponding retentions for the unacetylated fabric.

The elongation-at-break values for the unacetylated fabric decreased proportionately to the loss in breaking strength after steeping in acid solutions. On the other hand, as the severity of the acid treatment was increased, the elongation at break for each acetylated fabric increased to a maximum before decreasing to values below that of the untreated fabric. In general, the higher the original acetyl content, the greater was the loss of acetyl before the reduction in elongation was observed. The data after alkaline treatments indicated a relationship different from that shown by the acid treatments, but was not sufficiently complete to establish this conclusively.

In contrast to a previous finding that heat resistance of partially acetylated cotton, as measured by a 4-day test in dry air at 160° C., is as effective when the acetyl content is 11% as at 28% [6, 7], the present results show that the acid resistance is markedly greater at higher acetyl contents.

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The Effect of Temperature on the Physical and Chemical Development of Cotton Fiber

Lyle E. Hessler, Carole R. Simmons, and Harry C. Lane[1]

Texas Technological College,[2] *Lubbock, Texas*

INCREASED accuracy in measuring fiber properties has focused attention on cotton fiber development in recent years. Only under favorable environmental conditions will any given variety of cotton reach full development. Of the environmental conditions influencing fiber development, temperature plays a predominant role by affecting the rate at which plant metabolic functions proceed during development. High temperatures slow down fiber development by denaturization of the fiber cell plasma protein and inactivation of the enzymes functioning in cellulose synthesis. Temperature in the cotton boll can very well rise to 120° F. on hot days, as shown by Anderson [1]. That physical properties will also be affected by heat has been demonstrated by Hessler [4] where excessive heat affected cotton fiber development by producing fiber of shorter length, lower fineness, and greater strength.

For a number of years the Cotton Division of the U.S. Department of Agriculture conducted extensive regional variety tests on cotton. The tests show the effect played by environment on the fiber properties and spinning performance of cotton. These data have been summarized in the U.S.D.A. publication *Better Cottons* [13].

Since every biological reaction has an optimum temperature for rate of reaction in biological function, any temperature below the optimum will slow down plant processes. O'Kelley [12] in studying the effect of temperature on cotton fiber elongation concluded that at low temperatures, cell elongation was limited by enzyme controlled chemical reactions, thus slowing the physiological processes and causing a cessation of fiber development.

Cross sections of cotton fiber by Anderson and Kerr [2] indicated a more dense deposition of cellulose next to the primary wall where fiber development was taking place under more favorable temperatures. As the fiber filled out its secondary wall in the cooler development period, the rings became less dense, suggesting a slowing down of cellulose synthesis. They also were able to demonstrate that under constant temperature (30° C.) and light, rings were not visible.

An effort has been made to study cotton fiber development under progressively decreasing seasonal temperatures. Chemical and physical properties of the cotton are presented along with fiber development characteristics as influenced by temperature deficiency of growth.

Materials and Methods

The cottons used in this experiment were standard varieties grown in the Lubbock, Texas area, crop of 1955. Moderate irrigation was used and the plants were never under excessive stress for water. Typical agricultural practices were used in planting, cultivation, etc. The cotton was sampled by taking a number of bolls from random plants at a predesignated position on the plants for each blooming date. The tests were made on two varieties in the same area. The data are reported on one variety, however; tests were made on strength, fineness, cellulose content, crystallinity, and degree of polymerization which indicated the data reported are reproducible under the same temperature conditions.

Micronaire fineness and Pressley strength were measured according to standard methods and under standard conditions of temperature and relative humidity. The Micronaire reading on blooming date [9–12], which was below scale, was determined by estimation.

Degree of polymerization, crystallinity, and dye absorption were measured according to methods described by Hessler and Upton [5] with the exception of DP where the samples were boiled in NaOH for 1 hr. to free the fiber of extraneous material prior to nitration.

[1] Department of Plant Physiology and Pathology, Texas Agricultural Experiment Station.

[2] Fiber and Spinning Laboratory of the Cotton Research Committee of Texas.

Cellulose determination was by the Kurschner and Hoffer [8] method where the sample was boiled for 1½ hr. in a mixture of 1 part of HNO_3 and 4 parts of alcohol. The digested samples were filtered in fritted glass crucibles, washed in 95% hot alcohol followed by isopropyl ether, dried, and weighed. Ash was found to be nil by determination and was neglected.

Statistical treatment was as follows: Correlation coefficient r was obtained from the standard procedure

$$r = \frac{\text{covariance } (xy)}{\sqrt{\text{variance } x \cdot \text{variance } y}}$$

The significance of the correlation coefficient was based on the formula for t where

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}}$$

for a small number of samples. This may be considered a critical test for significance.

During the time bolls were growing, air temperature records were made by a continuous thermograph. By means of a planimeter, the number of degree-hours below 70° F. was determined. The average number of hours below 70° F. during the six-week boll period is reported.

The boll period may vary, depending on the temperature of development, from 40 to 60 days. For this reason a boll period for development was chosen as six weeks and the degree hours per week below 70° F. were put on an average weekly basis for the six-week period of maximum boll development. The temperature base of 70° F. was chosen because below this region, plant functions slow down and in some instances cease, thereby interrupting cellulose synthesis.

In controlled temperature experiments O'Kelley [12] established that 15-day-old bolls showed a fiber elongation of 11.3 mm. at 72° F. and only 0.9 mm. at 59° C.

Results

The temperature deficiencies in Table I progressively increase as the boll development period extends into late season. Chemical and physical properties of the samples tested decrease with temperature deficiency with the exception of dye absorption which reaches a high positive correlation coefficient of 0.95 (Table I). Micronaire fineness was significantly correlated with temperature deficiency during boll development ($r = -0.95$). Strength of fiber was not significantly correlated with adverse temperature of development ($r = -0.81$); however, there was a loss in strength of more than 10,000 p.s.i. from the early to the late grown cotton. The highest correlation coefficient involving temperature in the experiment was with degree of polymerization or cellulose chain length ($r = -0.97$). Crystallinity and cellulose content of the fiber gave correlation coefficients which were negative and significant to the 5% level, whereas the three high correlations which are double starred were significant to the 1% level (a probability of this correlation being due to chance are only 1 in 100 times).

TABLE I. Physical and Chemical Properties of Cotton Fiber Developed under Progressively Lower Seasonal Temperatures—Crop 1955

Blooming date	Temperature[a] deficiency	Micronaire fineness	Cellulose, %	Degree of polymerization	Crystallinity, %	Strength, 000's lb.	Dye adsorption, %
8–8	303	4.1	94.8	7564	86.3	74.7	0.46
8–15	415	4.1	94.9	7340	86.3	79.3	0.51
8–22	527	3.6	94.4	7220	81.4	73.1	0.58
8–29	825	2.6	93.6	6630	78.7	70.7	0.63
9–5	1129	2.6	90.0	6090	78.6	68.7	0.69
9–12	1465	2.2	76.4	6125	77.7	69.3	0.71
Correlation coef. (r) with temperature and		−0.95	−0.89	−0.97	−0.88	−0.81	+0.95
t value		6.10**	3.91*	7.98**	3.71*	2.73	6.10**
$P = 0.01$	$t = 4.60$**						
$P = 0.05$	$t = 2.78$*						

[a] Average degree hours per week below 70° F. for six-week period.
* Values which are questionable because of the limited numbers of samples.
** Values which are considered significant.

TABLE II. Correlation Coefficient (r) of Various Chemical and Physical Properties of Cotton Fiber Grown under Decreasing Seasonal Temperature

Cotton fiber variates, X		Y	Correlation coefficient, r	t value: $p=0.01$ $t=4.60$** $p=0.05$ $t=2.78$*
Fineness	and	Cellulose	+0.55	1.32
Fineness	and	Crystallinity	+0.95	6.10**
Fineness	and	Strength	+0.89	3.91*
Fineness	and	Dye adsorption	−0.95	6.10**
Crystallinity	and	Dye adsorption	−0.96	6.79**
Crystallinity	and	Strength	+0.92	4.67**
Cellulose	and	Strength	+0.58	1.42
Degree of Polymerization	and	Strength	+0.85	3.23*
Degree of Polymerization	and	Crystallinity	+0.91	4.39*
Degree of Polymerization	and	Cellulose	+0.77	2.41
Degree of Polymerization	and	Fineness	+0.95	6.10**

* Values which are questionable because of the limited numbers of samples.
** Values which are considered significant.

Some correlations were determined on various physical and chemical properties of cotton grown under adverse temperature conditions (Table II). For instance, fineness was correlated with crystallinity ($r = -0.95$) and dye absorption ($r = -0.95$). Fineness and strength gave a positive correlation ($r = +0.89$). Crystallinity with dye absorption gave a high correlation coefficient ($r = -0.96$) and crystallinity a high correlation with strength ($r = +0.92$). The correlation of degree of polymerization with fineness was significant ($r = -0.95$). Strength and crystallinity were correlated with DP to a lesser degree ($r = +0.85$ and $r = +0.91$), respectively.

The relationship between dye absorption and fiber structure, as measured by crystallinity and fiber fineness at decreasing temperatures of fiber development, is shown in Figure 1. The dependence of fiber strength on cellulose chain length and order in deposition, as influenced by fiber development under temperature deficiency, is shown in Figure 2.

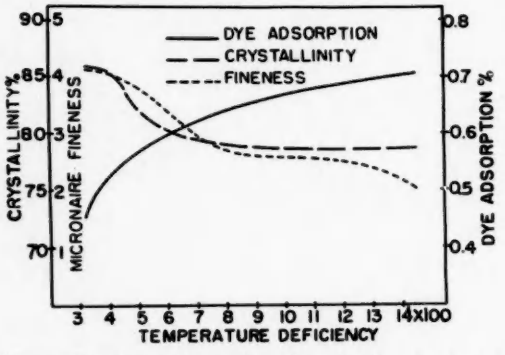

Fig. 1. The change of dye adsorption with fiber structure of cotton developed under temperature deficiency.

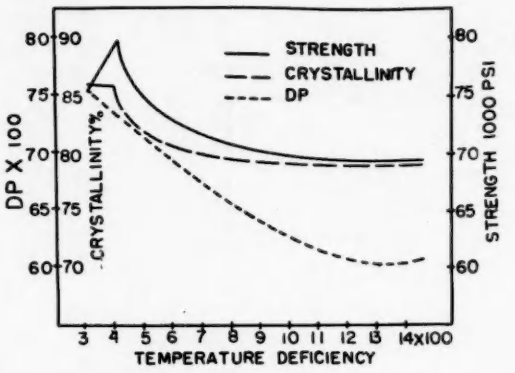

Fig. 2. The influence of fiber structure on strength of cotton developed under temperature deficiency.

The values for t as used for a test of significance are shown in the tables. The test for significance was used at only two levels, 1 and 5%. Values which are double starred in both tables may be considered significant, whereas those which are single starred may be questionable because of the limited number of samples.

Discussion

Ideally, the perfect climate for growing cotton is never realized. However, the optimum climate for developing a cotton fiber may be approached by some sections of the cotton belt in certain years. The habitat of the cotton plant is semi-tropical and the plant requires warm days and relatively warm nights for good development. Any temperature below 70° and above 100° F. will affect the functions of the plant and slow down fiber development. Of the many varieties grown throughout the cotton belt many have been developed by breeders in an effort to obtain the best genetic constitution for a given set of climatic conditions. Genetic variations in cotton with respect to plant reactions to environment are large but environmentally influenced variations within a single variety are nearly as great [3].

A survey of the early and late pickings in the summary report on fiber properties, crop of 1955, by the U.S. Department of Agriculture [14] indicates that over the entire cotton belt the early cotton is stronger and coarser in about 75% of the cases regardless of location. A previous study [6] indicates that as the boll period progresses through lower temperatures, the fiber becomes thinner walled and perimeter in-

creases. Table I substantiates a lack of development of fiber maturing under a temperature deficiency. A diminishing cellulose content discloses more of the constituents of the primary wall (low cellulose) in proportion to the secondary thickening (cellulose). The decrease in degree of polymerization and crystallinity at lower temperatures indicates less organization in the deposition of cellulose [2] and consequently, a weaker fiber. The high correlations between crystallinity and strength, and DP and strength were evidence of irregular deposition of cellulose. Analytical work on cellulose in developing bolls during low temperatures showed a decrease in cellulose, indicating that cellulose synthesis slowed down as temperatures diminished late in the boll period. Cellulose decreased in the boll from 1014 to 258 mg./boll from early to late boll development [9]. Thin layers of cellulose intermittently deposited during low temperature development can only mean a loose network of fibrils [2]. By actual tests (Table I), cotton developed under low temperature is lower in crystallinity (loose structure), shorter in cellulose chain length (underdevelopment) and weaker. Orientation of fibrils and size of crystallites must also be taken into account in evaluating strength and elongation of cotton fiber. Cottons with high X-ray angles are generally found in areas of slow development or low temperature environment [7]. Greater porosity and lower density measurements on immature cotton indicate loose structure for fiber development under adverse growing conditions [15]. A fast-developing fiber cell under optimum growing conditions produces a cotton of low spiral structure, a high degree of polymerization and high crystallinity, properties which favor strong fiber of good utility [7].

Many properties of cotton fiber are based on crystallinity. The ratio of crystalline to amorphous cellulose, the size of the crystallites, and their orientation all enter into the physical behavior of cotton. Besides the structural differences in cotton due to crystallinity, other associated differences in fiber properties based on crystallinity are the effects of moisture absorption. In certain types of crystallinity a high moisture content in the fiber may increase the amorphous fraction by changing some crystalline areas into more accessible ones [11]. These areas may even become permanent through the formation of cellulose hydrates which resist drying under fairly high temperatures. Most of the above mentioned fiber properties will vary through moisture adsorption which in turn is correlated with degree of crystallinity. Therefore, the crystalline-amorphous ratio of cotton fiber is a dynamic property which may change with the aqueous fraction of the fiber to give physical properties of varying degrees [16]. Fortunately, because normal, well-developed cotton has a high degree of crystallinity the properties affected by water adsorption are fairly stable. In confirmation of this is the high wet strength of highly crystalline cotton (86%) as compared with the low wet strength of low crystalline rayon (45%).

The degree of association of properties adds meaning to fiber behavior under present day processing for yarn and fabric (Table II). The solution to many problems of dyeing and finishing may also be found in this table. Direct dye uptake increases due to a greater amount of amorphous cellulose or loose structure as is found in cotton developed under adverse temperature deficiency. Furthermore, fine cotton grown under these conditions has thin walls and more irregular surfaces which produce optical differences, giving the effect of light shade appearance. Thus in the case of the late season cotton two properties affecting dye shade will be opposing each other, which often result in irregular appearing fabric. Figure 1 shows the relationship of dye adsorption, crystallinity, and fineness as influenced by temperature deficiency of fiber development.

The ability of fabric to adsorb moisture is essential in summer wear and is a function of fiber structure as well as fabric structure. Water adsorption is well correlated with crystallinity. Underdeveloped fiber of low crystallinity takes up water more readily than a highly crystalline fiber [16]. The advantages that may be gained by using cotton of low crystallinity in fabrics requiring rapid water adsorption could be many and need investigation.

Cotton growth under adverse environment indicates an interrelation of structural development based on reactions which influence the deposition of cellulose in the expanding fiber cell. If fineness is influenced adversely by low-temperature development then strength also is affected unfavorably. Thin wall fineness is strictly an underdevelopment characteristic, whereas strength deficiencies are the result of disorder in fiber structure as measured by spiral structure, low crystallinity and degree of polymerization [7], Figure 2.

How cotton withstands the stress and strain of spinning and weaving is associated with fiber crys-

tallinity (elongation) and strength relationships. A more elastic fiber and yarn, if not too weak, weaves with less difficulty. Finally, the influence of environment and the association of properties may be used to predict luster of fiber and the response of cotton to mercerization and ultimate light reflectance [10].

Summary

In a study of cotton fiber development under low temperatures, high correlation coefficients were found between temperature deficiency of fiber development and fiber fineness (-0.95), degree of polymerization (-0.97), and dye adsorption ($+0.95$). Correlations were established to a lesser degree between temperature deficiency of development and cellulose content (-0.89) and crystallinity (-0.88).

High correlations between fiber properties of cotton developed under adverse temperature were found between fineness and crystallinity ($+0.95$), fineness and dye adsorption (-0.95), crystallinity and dye adsorption (-0.96). Other correlation coefficients were noted between fineness and strength ($+0.89$), degree of polymerization and strength ($+0.85$), and degree of polymerization and crystallinity ($+0.91$).

Cotton development under a temperature deficiency shows irregular microstructure as measured by crystallinity and dye adsorption. Cellulose content of the fiber and cellulose chain length decrease with development under lower temperatures. Fiber wall thickness as measured by fineness also decreases, which shows further lack of fiber development. Strength of fiber, while not highly correlated with temperature deficiency, is affected adversely.

The interrelations between fiber properties from cotton developed under low temperature can be used to predict cotton behavior in processing, dyeing, and finishing.

The relationship between cotton fiber development and structure is established through wall thickness (fineness), crystallinity, and cellulose chain length measurements. The importance of fiber structure (crystallinity) in relation to properties and fiber behavior is emphasized.

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Letters to the Editor

An Improved Fiber Rotator[1]

Canada Department of Agriculture
Experimental Farm
Lethbridge, Alberta, Canada
January 30, 1957

To the Editor
Textile Research Journal

Dear Sir:

When studying the surface structure of textile fibers or when determining the fiber cross-sectional area by nondestructive means, it is necessary to mount the fibers so that they may be rotated along their longitudinal axis in the field of a high power microscope. A research program carried out in this laboratory, which involved the microscopic study of the surface morphology of wool fibers at predetermined points, called for an instrument satisfying the following requirements:

a. Satisfactory centering of the fibers ensuring that the image will remain in the visual field of the microscope, and preferably in focus, while being rotated or traversed laterally.

b. Adjustable jaw distance so that small forces necessary for decrimping or stretching may be applied to the suspended fiber.

c. Small size, enabling the instrument to be mounted on the mechanical stage of the microscope.

d. Speed and convenience of handling.

Since none of the commercially available rotators appeared to be suitable for our purpose, a simple but efficient instrument employing magnetic chucks instead of the conventional clamps was designed and built in our workshop. The purpose of this note is to outline the construction and use of this instrument (Figures 1 and 2).

A caliper with a maximum jaw distance of 5 in. was employed as the base of the instrument. A model was chosen with a sliding jaw which could be locked securely in place by means of a thumb screw. Both the stationary and sliding jaws were fitted with brass bearing housings to accommodate the small ball bearings for the rotator shafts and drive shaft, respectively. Parallel alignment of the housings was found to be essential. To ensure greater stability of the rotator shafts, twin ball bearings were employed. A simultaneous and equal rotation of the two independent chucks was effected by means of gears attached to the rotator and drive shafts.

The proximal ends of the rotator shafts were fitted with flat, slightly U-shaped, permanent alloy magnets. It was important that the surfaces of the magnets be finely polished and parallel. The fiber holders were made of soft iron and were attached to the shafts by magnetic force. The shape of the fiber holders will depend on the type of work to be performed. In our work, small flat discs, fitted with needles at the center, have been used and found very satisfactory.

The advantages of the magnetic chuck in an instrument of this type, where accurate centering of the object is required, are obvious. In conventional rotators the fiber is cemented either to the rotating shafts or, preferably, clamped in chucks rigidly fixed to the shafts. In either case it is extremely difficult to mount the fiber centrally. Eccentricity cannot be

[1] Contribution from the Division of Animal Husbandry, Experimental Farms Service.

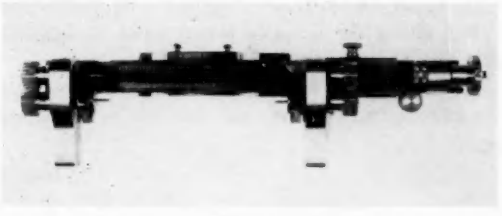

Fig. 1.

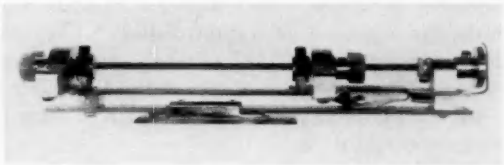

Fig. 2.

corrected once the fiber has been mounted, and will cause the fiber image to move out of the field and out of focus while being rotated, especially under high power magnification. With magnetic chucks the proper attachment of the fiber to the holders becomes unimportant. The centering is done after the fiber has been attached to the holders, and any inaccuracies in the mounting may be compensated for easily by sliding the holders gradually into the required position. It should be pointed out that forces applied for decrimping or stretching of the wool fiber are insufficient to alter the position of the holders once centering is completed.

The mounting and centering of the fiber are performed as follows:

The ends of the fiber are drawn through the eyes of the needles and secured in place with a minute drop of quick-drying cement. The fiber then is decrimped by widening the distance between the caliper jaws, and a coarse centering of the holders is made macroscopically. Fine adjustment is performed under the microscope using low power (30 to 50 ×), and, if necessary, it may be further corrected at higher magnifications. In performing this operation the fiber segment adjacent to the holder is brought into focus, and the holder adjusted manually until the deviations of the rotating fiber from the center line of the field become negligible. When both ends of the fiber are centered in this manner, a satisfactory alignment of the entire fiber is assured.

Provision was made for moving the entire instrument longitudinally under the microscope by attaching a guide plate to the lower surface of the instrument. This guide plate fitted into a grooved holder. The latter had the same dimensions as a standard microslide and thus could be clamped conveniently into the slide holder of any standard mechanical stage. Through this arrangement the range of traverse was extended, and fibers longer than the maximum travel of the mechanical stage could be studied along their entire length.

Acknowledgments

Thanks are due to Mr. A. H. Woolliscroft for helpful suggestions in developing this instrument.

E. C. BANKY [2]
S. B. SLEN

[2] Deceased.

The Diffusion of Water Vapor through Laminae with Particular Reference to Textile Fabrics

Defence Research Medical Laboratories
Toronto, Canada
February 11, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

We wish to correct an error of statement which appeared in a communication submitted by us on "The Diffusion of Water Vapor through Laminae with Particular Reference to Textile Fabrics" [TEXTILE RESEARCH JOURNAL **25**, 197 (1955)]. In this paper we gave in Equation 1 (and repeated in Equations 6, 7, and 8) the resistance of an air space in units of thickness of still air as

$$R = (DAt/Q)(p_a - p_b)$$

where p_a and p_b were stated to be vapor pressures. These latter should be vapor concentrations. Calculation of the experimentally determined value for D, the diffusion coefficient of water vapor in air, by the method described, requires the use of vapor concentrations rather than vapor pressures. Concentrations were in fact employed in arriving at the results given, the values of vapor pressure (known values of relative humidity and temperature) being converted to water vapor concentrations by the use of Smithsonian Tables giving the mass of water vapor in saturated air over a range of temperatures.

We are grateful to have had this error brought to our attention and to have the opportunity of correcting it.

L. E. MACHATTIE
A. C. GOODINGS
L. H. TURL